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Properties and Effects of Rinse Water Additives on the Corrosion Rates of Structural Metals Used for Marine Corps Ground Vehicles

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14. ABSTRACT

Corrosion of military equipment remains a serious problem. It affects both operational readiness and life cycle costs. Commercial additives have been proposed for inclusion in fresh water rinses used to inhibit corrosion of military vehicles exposed to marine environments. The performance data available for these products are qualitative and do not permit reliable assessment of their utility or the anticipated level of protection. Investigation of the problem is complicated by the fact that during operations, military vehicles usually experience a wide range of environments that influence corrosion behavior. This work investigates the properties of commercial rinse additives and their influence on the corrosion rates of aluminum and steel samples. The properties examined were the ability of additives to affect seawater-induced corrosion processes, the level of inhibition observed as a function of salinity of seawater, and adherence of additive to the metal surface. An attempt was made to establish a basis for predicting and ranking the value added by wash additives during practical application.

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PROPERTIES AND EFFECTS OF RINSE WATER ADDITIVES ON THE CORROSION RATES OF STRUCTURAL METALS USED FOR MARINE CORPS GROUND VEHICLES

EXECUTIVE SUMMARY

Corrosion of military equipment and infrastructures continues to be a significant problem for the U. S. Military. A recent report estimates the cost of this problem to be $20 billion annually to the Department of Defense.[*] A considerable portion of these expenses, $2 billion, are attributed to ground vehicles used by the Army. As a specific example, in 1997 it was estimated that the cost to replace corroded frame-rails on HMMWVs owned by the U.S. Marine Corps at one facility was $4.2 million. Corrosion related failures therefore adversely contribute to life-cycle cost, operational readiness and high manpower and resource waste.

For the past six years a group of Naval Research Laboratory (NRL) scientists have been supporting the Marine Corps in developing methods of corrosion control for ground vehicles (principally HMMWVs) and light weapons systems. Their investigations include extensive interactions with the Marines during site visits to MARCORPAC, MARCORLANT, and participation in military exercises at 29 Palms and the Marine Corps System Command CPAC meetings. These interactions served well to identify and accurately describe significant corrosion problems and to establish boundaries for solutions that could be immediately applied in the field.

This report concerns a laboratory assessment of the value of using commercially available additives (originally designed for corrosion control in the boating and fishing industries) during operational and maintenance flushes intended to remove seawater and provide corrosion protection to ground vehicle structural metals, specifically, aluminum and steel. This approach is being investigated by maintenance personnel on Marine Corps bases. The NRL experimental work was designed to minimize variables and assure the presence of the additive during seawater exposures. In this way it was possible to observe whether a reduction in corrosion occurs and rank the performance of several additive products. No attempt was made in this study to evaluate the endurance of the additive effects after drying and repeated seawater exposures as would be encountered during operations. In scientific parlance this work represents "proof of concept" testing or accelerated testing.

The most important findings of this study are:
(a) In aluminum, pitting is significantly increased in seawater containing some of the additives and rinses containing these additives should be avoided for aluminum parts. In the presence of ADD4 and ADD2, aluminum pits less than in unaltered seawater and these additives may be recommended for aluminum.
(b) Some of the additives provided poor protection to steel in seawater and these additives may be avoided. However significant reductions in corrosion rates are observed in diluted

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[*]"Corrosion Cost and Preventative Strategies in the United States," FHWA-RD-01-156, U.S. Department of Transportation, Federal Highway Administration, March 2002.
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seawater and in ADD4, ADD3 and ADD2 containing seawater, and these additives may be recommended for steel.

(c) ADD4 and ADD2 may be recommended as wash additives for both aluminum and steel.

(d) Laboratory tests show some correlation with the results of long-term field tests emulating a plausible seawater exposure scenario.

(e) Rinse additives show different inherent levels of adherence and modifications to the surface conditions at a metal-seawater interface from SPR.

(f) Using the results from this study as a base line, follow-up work should examine the adherence of rinse additives once the aluminum and steel surfaces are dried and re-exposed to seawater as a simulated field condition.

INTRODUCTION

Operational maneuvers for military ground transport vehicles routinely include submersion in seawater and prolonged exposures to salt spray. Residual salt deposits combined with humidity during downtimes or storage promote the accelerated deterioration of metal components. As a result it has been shown that the operational lifetimes of military vehicles can be reduced by more than 30% and the costs for replacing individual damaged parts can be greater than 10% of the initial cost of the equipment.[1-4] Corrosion is a significant problem for all branches of the military because it affects readiness and life cycle costs of the operational equipment.[5] In order to remedy the problems associated with corrosion, maintenance facilities on military bases are exploring the use of commercial inhibitor additives to augment the recommended procedure for fresh water rinses following exposure of the vehicles to a corrosive environment. It should be noted that fresh water rinses are not always practical for the military because of time constraints of an active military operation and uncertainty in the availability of fresh water. Many inhibitor additives have been suggested. However, evaluations of the appropriate treatments are complicated by the fact that it is very difficult to construct a "typical" set of conditions for exposures of military equipment to saltwater or salt spray environments. Furthermore, there is little quantitative data supporting the degree of effectiveness of each additive. In addition, for proprietary reasons, neither the additive ingredients nor details of their function are available so a credible evaluation cannot be made.

There is a pressing need to establish baseline information concerning the effects of water rinses on vehicular corrosion. In an earlier study, Bierberich and Sheetz[6] measured the weight loss of metal panels exposed to marine environments. These panels were subjected to fresh water wash down at one or two week intervals for one year and weighed before and after the tests. Their results showed a decrease of up to 30% (in the case of the weekly wash down) in the corrosion rate (weight loss) of saltwater-exposed steel periodically washed down with fresh water. As expected, the corrosion rate was less for a more frequent wash down cycle. With somewhat less precision, this work showed that the depth of pits on aluminum was lower as a result of the fresh water washes. The study also included evaluation of the effects of rinses that included additives on corrosion rates for the same experimental conditions. Results showed that the additives could improve the benefits of water rinses and that the degree of protection depended upon the additive. While Bierberich and Sheetz's[6] assessment of the effects of additives was exhaustive (tests were replicated and performed in a broad range of test environments), significant variations were observed between individual results. These variations are characteristic of weight loss measurements, however, and were compounded by unmeasured and, therefore, unknown changes within the marine environments. Temperature, humidity and composition of the environment are factors that can introduce a level of uncertainty to the solution of the problem of assessing the effectiveness of the additives. Nevertheless, weight loss experiments constitute a direct measure of corrosion rates and a statistical analysis of the results can show useful trends. Correlating weight loss results with other results, e.g., electrochemistry results, can mitigate the uncertainty.

APPROACH

In this work, the fundamental properties of wash additives relevant to their application for corrosion control are examined through a series of laboratory-scale studies. In particular, the ability of the additives to inhibit the corrosion processes, especially in variable saline conditions, and their degree of adhesion to the metal surfaces were examined. Because of the high degree of variability shown by inhibitor activity, the analysis, by design, is statistical in nature. The objective is to use statistical information and correlations to establish a database of fundamental inhibitor behavior that can be exploited to develop reliable assessments of their benefits in field operations. The corrosion rates of metal samples immersed in artificial seawater containing recommended dosages of additive were determined. The corrosion rate was measured as weight loss. Several additives were evaluated. Aluminum alloy 6061 and 1018 steel specimens were selected because they are representative of the main structural materials in the construction of Marine Corps vehicles. Furthermore, the results could be compared to the outdoors marine exposures discussed earlier. The experimental set-up was not meant to mimic field conditions but rather to isolate conditions that are controllable and to assure the presence of the inhibitor additive against the metal. In this case the inherent ability of the additive to affect corrosion processes of each metal in seawater could be observed. The experiments were repeated with diluted seawater. This case represents the effects of the additives in reduced strength salinity as for example when the metal surface is rinsed of seawater. These conditions test the assumption that watered-down seawater may prove to be beneficial in instances when fresh water supplies are limited.

Weight loss results were supplemented with another study involving surface plasmon resonance (SPR) spectroscopy. SPR is a surface sensitive optical reflectivity technique widely used for the study of the adsorption and character of organic and inorganic molecular layers (tens of angstroms thick) on metal surfaces. SPR was investigated as a method to examine the fundamental adherence tendency or sticking of the additive or its components to the metal surface. Surface plasmons are the aggregate of free electron oscillations in a metallic film. When the free electrons are set to oscillate (resonate) with an incoming light source, light energy is absorbed which results in changes in the reflectivity of the incident beam off the surface. The resonant condition is very sensitive to the local refractive index at the surface and so the adsorption of molecular species (whose character affects the refractive index) can be accurately detected. An understanding of the adhesion properties accompanying the additives will provide figures-of-merit for establishing inhibitor performance and important clues to the processes occurring at the metal surface. This study represents a preliminary analysis of adherence properties of inhibiting washes using a "surface specific" method based on optical reflectivity measurements. Such an approach is similar to that of Klenerman and coworkers, who studied the deposit of oleic imidazoline derivatives on steel in seawater using second harmonic generation (SHG) reflectance measurements.[7-9] In the present study we use SPR to explore the natural attraction or tendency of the additives to adhere to and distribute over metal surfaces. Another aspect of our approach is that it is based on the use of features that provide for a statistical interpretation of the reflectivity measurements. This approach was applied in a series of studies concerning the analysis of SHG measurements of reflectance from metal-electrolyte and thin film interfaces.[10, 11]

EXPERIMENTAL PROCEDURES

Immersion tests

Standard immersion tests, described in detail elsewhere,[12] were used to study the effects of the commercial inhibitor additives on the corrosion behavior of 6061 aluminum and 1018 steel specimens in seawater. Corrosion rates were determined as weight loss measurements. We evaluated six commercial additives. In order not to reveal the identity of the products, we denote the inhibitor additives, listed in Table 1, as ADD1 to ADD6. The manufacturer's description of each additive and recommended dilution level is also given in Table 1. Test samples were 1-inch (2.54 cm) x 2-inch (5.08 cm) x 1/8 inch (0.32 cm) coupons sectioned from test metal panels. An eighth inch (0.32 cm) diameter hole was drilled at one end of each coupon to suspend it, using a nylon thread, from a plastic lid into a 200 ml glass jar. A quarter inch (0.64 cm) diameter hole was drilled into the top of the lid for venting. All samples were rinsed sonically in methanol, dried and stored in a desiccator until the tests were started. Figure 1 shows a photograph of the experimental set-up for the immersion tests.

Artificial seawater was prepared by adding 4 oz of a synthetic sea salt Instant Ocean,[*] to one gallon of distilled water. This was adopted as full strength or full salinity seawater. Solutions of the artificial seawater and the manufacturer's recommended wash-additive dosage were prepared. Exactly 200 ml of these solutions was added to the test jars. The metal samples were weighed, dipped in seawater for 2 minutes and then suspended in the test solution for 3 months. Distilled water was added to the jars weekly to adjust for losses due to evaporation of water. At the end of the 3 months, the samples were removed from the solution, rinsed with distilled water, and the corrosion products removed following standard procedures.[12] The samples were then thoroughly dried, weighed, and the change in weight determined. Additional tests were performed by adding the manufacturer's recommended dosage of the additive to stock solutions of artificial seawater diluted to half and quarter strength with distilled water. By this means, the salinity of the test solutions was varied. Each test was repeated in triplicate to assess reproducibility of the results and to bring about a robust statistical analysis. In addition to measuring the weight loss, the exposed samples were visually examined and photographed. Reaction products on the metal surface were noted and in one case an attempt was made at identification.

Surface plasmon resonance (SPR) spectroscopy

A 2.2 cm² cover glass was cleaned with a hot "piranha" solution (30:70 v/v mixture of H_2O_2 and H_2SO_4). A 50 nm gold film was deposited onto the cover glass from a gold coin (99.99%) using a vacuum evaporator. Deposition was in a vacuum of 10^{-6} bar and at a rate of 0.02-0.04 nm s^{-1}. The gold film thickness was determined using a crystal oscillator. Inhibitor additive layers were applied to the gold-coated cover glass slips by spin coating each liquid additive at 8000 rpm for 60 s at room temperature. The additive-coated surfaces were then ready for SPR analysis. In some experiments, the additive-coated substrates were washed with either distilled water or 1% NaCl for 5 min prior to performing SPR analysis. The SPR spectrometer used for analysis employed the Kretschmann configuration,[13] a schematic of which is shown in

[*] Aquarium Systems, Inc., Mentor, OH.

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Figure 2. Here, a prism is used to couple the wave vectors of the incoming light beam with that of the plasmons. The glass prism was made of standard BK7 glass (90 degrees, 17 mm high, 22 mm by 32 mm at the base, refractive index n = 1.5). Index matching fluid was used to index match the prism to the cover glass (n=1.51). The SPR instrumentation consisted of a semiconductor diode laser (HeNe, 1.0 mW, p polarized at 632.8 nm) as the light source. The polarized light is incident on the prism and reflected back from the base of the prism onto a photodetector. Variable angles were selected by means of a stepper motor controlled goniometer with a resolution of 0.1 degree. The data acquisition was completely automated, with a typical SPR scan angle (40° to 80°) taking 8 minutes. SPR scanning angle experiments, used in this study, follow reflectivity as a function of the angle of incidence of a light beam focused on a metal surface. Observed changes in reflectivity are used to examine the attraction and adherence of rinse additives or their constituents to the metal substrate. The specific mode of analysis adopted in our study is that used by S. S. Yee and coworkers[14-18] to study the nature of organic films on gold surfaces. In the present study, a gold substrate was selected for SPR testing of all additives as well as the seawater control. The use of gold is preferable for an examination of the inherent tendency of inhibitor additives to adhere to metal surfaces. It is assumed that minimal electrochemical events will occur at a gold surface in the test solutions used.

The simplest interpretation of physical processes underlying SPR is of surface plasmons as surface waves which propagate through a medium consisting of free electrons of a given density distribution and relative mobility. These surface waves are induced by an incident light beam of given wavelength as shown in the schematic diagram in Figure 3. The free electrons that support the surface plasmons are interpreted as moving in a polarizable and screening background, which is associated with the bulk metal substrate. Any external influence, which modifies the physical characteristics of this background or of the free-electron density distribution, will affect the characteristic mobility of the surface electrons and thus the oscillatory structure of the plasma waves. In particular, any external influence, which tends to constrain the characteristic mobility of the surface electrons, will tend to dampen the surface plasmons. This simple interpretation is sufficient for our analysis of adherence properties of inhibiting washes. For our analysis we consider changes in the density distribution and mobility of surface electrons supporting surface plasmons. Specifically, there is a direct correlation between the absorptive part of the complex refractive index or absorbance character of a sample layer and the amplitude of the resonance minimum observed in the reflectivity as a function of angle of incidence (or of reflection).[14]

EXPERIMENTAL RESULTS

Weight loss

The raw data for weight loss measurements are given in Table 2 for the aluminum and steel samples. The table includes the dates the experiments were started and concluded. For each sample, sample #, additive, dilution, strength of seawater, sample dimensions, sample weight before and after the test, difference in weight and percent weight loss are reported. From the replicated percent weight loss results, averages and standard deviations (S.D.) were calculated. These results are given in Tables 3 and 4 for the aluminum and steel samples, respectively. Furthermore, percent weight loss relative to that in unaltered seawater was

determined as ratio of weight loss in additive to weight loss in seawater control. These results are presented in Table 5. Values of less than 1.0 imply that the inhibitor performed better than unaltered seawater, values greater than 1.0 imply that the inhibitor performed worse than seawater. This was one way of examining the weight loss results assessing the merits or demerits of inhibitor additives. Another way was to rank the inhibitor additives, along with the seawater control, from lowest to highest percent weight loss. Three plots were made for the three different seawater strength levels for each metal. Plots in Figures 4 and 5 show the additive rankings obtained for aluminum and steel, respectively. In order to compare the influence of the various inhibitor additives on weight loss, the results were plotted as a function of seawater strength for the additives and seawater control. Figures 6 and 7 show the weight loss as a function of seawater strength for aluminum and steel, respectively. Results with additives having the least influence on weight loss were re-plotted to amplify their influence and are shown in Figures 6(b) and 7(b).

Several observations are made from these tables and graphs. Results differ significantly for the two metals. In general and not surprisingly, weight loss or corrosion rate was higher in steels compared to aluminum. The effect of the strength or salinity of the seawater on weight loss was ambiguous. For aluminum, the weight loss trend appears to increase with increasing seawater strength for some of the additives, but not for others. For steel, in additive dosed seawater the weight loss does not appear to have any predictable trend as a function of seawater strength, however a significant decrease is noted from full to half strength for unaltered seawater. Compared to the seawater control, some of the additives worsened the corrosion behavior for both metals. Instead of inhibiting corrosion, these additives appear to have enhanced corrosion. Other additives did improve corrosion behavior for both metals. This is clearly seen in the rankings of the inhibitor additives according to weight loss. The worsening or improvement in corrosion behavior and its magnitude varied widely among the additives. Additives that improved the corrosion behavior showed no particular trend with increasing seawater strength or salinity for both metals or, at the very least, the variations were within the error bars and, hence, statistically insignificant. ADD5, ADD6, and ADD1 were found to be detrimental to both metals. While ADD2 was found to be beneficial for aluminum, ADD3 and, to a lesser degree, ADD2 were found to be beneficial for steel. ADD4 was found to be beneficial for both metals, both in the recommended dosage as well as in 4 times the recommended dosage. There appears to be very little difference in the results between the two dosages of ADD4 for both metals.

Appearance of samples after exposure

We observe that exposure of the metal samples in the various inhibitor additive environments appears to have resulted in two specific modes of corrosion for the two different metals. The aluminum samples exhibited pitting-type corrosion. An example of the corroded surface of aluminum is shown in Figure 8. On the left is a coupon immersed in seawater containing ADD3. Note the isolated pits and the corrosion product around each. The steel samples exhibited general corrosion when corrosion was acute. An example of a corroded steel sample after exposure to seawater containing ADD6 is shown in Figure 9. Corrosion products appear to flake off the surface of the steel coupon. For all other samples the corrosion product was a rusted color and large portions remained on the surface. The corrosion product was collected and to identify it, x-ray diffraction analysis was performed. Figure 10 shows the x-ray

diffraction spectrum of the steel corrosion product. For comparison, a spectrum corresponding to the magnetite standard is superimposed on the graph. The close matching of the reflections indicate that the corrosion product on the steel sample immersed in ADD6 is magnetite or Fe_3O_4.

Surface plasmon resonance (SPR) spectroscopy

Surface plasmon resonance spectra of the gold substrate without and with additive coating and after washing the additive coated substrate with water and 1.0% NaCl are shown in Figures 11 and 12. The curves are of the reflected light intensity, the Reflectivity function, R, as a function of angle of incidence (the angle θ is shown in Figure 3). The procedures for substrate preparation and subsequent inhibitor additive coating of the substrate were the same for each of the measured SPR spectra. Factors contributing to variability of the SPR measurements are the relative levels of substrate surface roughness and inhomogeneities within the surface covering. Each measurement was repeated three times and there was good consistency in the replicated results. The data are presented in two sets and a gold baseline was set for each as shown in Figures 11(a) and 12(a). This is because the measurements were made on two different days and this is reflected in the different scales for R. We analyzed the data further by noting the position (scan angle) and the amplitude of the minima in the spectra. These results are presented in Table 6. From the results, we make the following observations. Runs with the two sets of bare gold ("no wash") substrates are similar, the minima positions being near 46.4 and the amplitude (-R) of the minima being 0.46 for the first set and 0.57 for the second set. The "water wash" curves also have minima at the same angle as the "no wash" gold. The "NaCl wash" curves also have minima, but at a higher scan angle. The gold substrates coated with the inhibitors had different responses to SPR spectroscopy. The "no wash" curves for ADD2, ADD3, ADD6 and ADD4 showed no minima. The "no wash" curve for ADD1 had a minima at a scan angle near that of bare gold, but with a reduced amplitude. The "no wash" curve for ADD5 was at a significantly lower angle and had a significantly reduced amplitude. After the "water wash" and "NaCl wash," minima appeared in all spectra. However, the position of the minima shifted by different amounts from that of the bare gold and the amplitude varied somewhat.

DISCUSSION

Weight loss and corrosion rate

The weight loss results show that the corrosion rate is influenced by the additives and, not surprisingly, is different for the two metals. The steel samples showed a higher rate of corrosion than the aluminum samples under similar conditions. To determine the magnitude of this difference, the ratios of weight loss in steel to weight loss in aluminum for the different additives and for seawater control and for the different seawater strengths were determined and are given in Table 7. As expected, in unaltered seawater, the corrosion rate of steel is greater than that of aluminum, the ratio varying from about 21 to 62, depending on the additive. This underscores the tendency of steel to corrode more readily than aluminum in an aqueous environment. In the presence of inhibitors, the results are similar in most cases. However, the magnitude of the steel to aluminum ratio varied depending upon the inhibitor. For instance, in the cases of ADD1, ADD6 and ADD5, this ratio varied modestly, from 1.4 to 2.8. In the case of ADD4, this ratio was several times but consistent, varying from about 43 to 47. However, in the case of ADD2,

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this ratio varied widely, from a low of 35 to as much as 372. The exception was ADD3, in which case this ratio was less than one for the higher seawater strengths and a little over 1.0 for the low seawater strength. The response of the steel samples to ADD3 appears to be comparable or even more favorable than the response of the aluminum samples to the same additive.

From a practical point of view the weight loss results clearly indicate the importance of informed inhibitor selection for metallic structures that will be used in a marine environment. It is clear that during total immersion in seawater, two of the additives tested, ADD4 and ADD2, affected significant reductions in the corrosion rate of both aluminum and steel as compared to the seawater control. Additionally, in the case of steel, ADD3 also affected reduction in the corrosion rate relative to seawater. The aluminum coupons showed no detectable pitting at the end of the three-month test cycle and the steel coupons showed very little surface attack.

The corrosion rate of aluminum remained essentially constant with increase in seawater strength or salinity when immersed in the unaltered seawater control. Seawater salinity independence, at least within the measurement error, was observed when ADD4, of both dilutions, ADD1 or ADD2 was added to seawater. When ADD3, ADD6 or ADD5 was added to seawater, corrosion rate increased with increasing seawater strength. In the seawater control, the corrosion rate of steel decreased significantly (by 50%) as the salinity of seawater was decreased by half, but remained essentially the same with further reduction in salinity. It is possible that lower strength seawater even without the additives can provide some benefit for steel when fresh water for a wash cycle is scarce. In steel, the presence of any of the additives in seawater appears to have produced no predictable trend with seawater strength. With some inhibitors, such as ADD1, ADD2 and ADD4, there appears to be a mildly increasing trend. With others, e.g., ADD5 and ADD3, there appears to be a mildly decreasing trend. These trends may not be statistically significant.

Analysis shows that for additives that worsen the corrosion response, the strength or level of salinity of seawater does influence weight loss in aluminum but not in steel. This is contrary to the observation that the level of salinity in unaltered seawater had no influence on aluminum, but did have an influence on steel. In this case, the seawater environment does affect the corrosion processes in aluminum but not in steel. It is possible that components in these inhibitors interact with seawater in such a manner as to produce the opposite effects observed on the two metals. For inhibitors that improve the corrosion response, the level of salinity had no significant effect on weight loss for either metal. This is a significant observation because it implies that seawater strength becomes less important when selecting a wash containing beneficial inhibitor additives.

In general, it is apparent that the action of the additive or its ingredients dominates the corrosion processes in both metals. Since additive ingredients are a trade secret, any explanation forwarded would be speculative. Relative to seawater control, some additives increase the corrosion rate by a large extent, some decrease the corrosion rate by a large extent. These results provide a ranking and some guidance for the use of the additives under field conditions. A couple of inhibitors were found to produce lower corrosion rates in both metals. This is significant because it meets the need to identify wash additives that would be suitable for both metals.

In aluminum, pitting is the dominant corrosion mechanism. Pitting of aluminum is known to initiate by some action of the chloride ion, at very small concentrations, leading to the breech of the protective Al_2O_3 surface film. With inhibitor additives that markedly increase the corrosion rate, more numerous, larger and deeper pits were observed on aluminum. These additives also show an increasing trend with increasing salinity. The extent of pitting, determined by examination, correlated well with the weight loss results for the different additives.

In sum, it can be concluded that of the inhibitor additives studied, some of them should be avoided categorically for both metals, a few are recommended, and a couple of these appear to be beneficial to both aluminum and steel. The conclusions from this study are in substantial agreement with the conclusions of Bieberich and Sheetz[6] who performed periodic wash-down cycle tests to evaluate the use of the wash down additives for corrosion control during marine environmental exposures. By and large some of their recommendations and rejections are in agreement with those of this work.

SPR spectrum analysis based on statistical feature variables

The density distribution and mobility of surface electrons represent characteristics that determine the strength of coupling between the incident light wave and the plasma wave transmitted along the surface of the metal substrate. It follows therefore that the amplitudes of plasma resonance minima may be adopted as a statistical feature whose magnitude may be correlated with the average adherence properties of adsorbates or of surface coatings in general. This follows since any form of physical adsorption at the metal surface will tend to constrain both the mobility and availability of free surface electrons.

The theory of SPR combined with effective medium theories for representing the electromagnetic permitivity of the substrate and inhibitor coatings provides, in principle, a formulation for the analysis of the different features associated with SPR spectra. These features would include, for example, relative shifts or broadening of SPR minima. This type of analysis would require, however, detailed information concerning the chemical composition of the inhibitor solutions, explicit knowledge of substrate surface roughness, the electronic nature of the absorbed molecules, the extent of surface covering by absorbed molecules and the statistical character of inhomogeneities within the surface covering. Our analysis considers, therefore, only one feature of SPR spectra, the relative amplitude of the minimum of the reflectivity function, a quantity that may be correlated with the density distribution and mobility of free surface electrons. The density distribution and mobility of surface electrons, in turn, may be correlated with the presence or absence of an inhibitor film on the substrate or with the relative average level of surface coverage by an inhibitor or with the relative ability of the inhibitor to adhere to the metal surface via some unique bonding mechanism. We emphasize again, as discussed in the above section, that the amplitudes of the SPR minima are to be interpreted as statistical feature variables rather than "deterministic" spectral signatures to be correlated with known structure of the additives or their components.

From the SPR results, it is observed that all additive coated ("no wash") gold substrates showed no minima except for ADD1 and ADD5. The response for these additives correlates with a coating layer having a relatively weak adherence to the substrate. A weak adherence of the coating layer to the metal substrate, such that surface electron mobility or availability is not reduced, implies that there is minimal constraining of the oscillations of the free electrons on the surface of the gold. The resonance amplitudes of the SPR minima associated with ADD2, ADD3, ADD6 and ADD4 are negligible or nonexistent. This "totally damped" response may be correlated with a coating layer that tightly adheres to the substrate. This implies a change in the density distribution of surface electrons which is sufficient for constraining, or rather, totally damping out any oscillations of the free electrons on the surface of the gold substrate.

Results of reflectivity curves corresponding to two different experimental trials involving washing of additive coated substrates using fresh water or 1% NaCl are interesting. It can be seen that, after washing, amplitudes of the SPR minima for the surface coated with the additives all obtain similar values relative to each other. In addition, these spectra all indicate a similar level of damping relative to the bare gold substrate. This consistency suggests that in each case water represents the dominant ambient medium at the gold interface. One observes that after washing with 1% NaCl, the amplitudes of almost all the SPR minima are large and shifted to a higher angle relative to those associated with bare gold. It is to be noted that for ADD3 and others there does exist a non-negligible level of damping of the SP resonance. This implies the persistence of some coating after washing. It is further noted that there is actually amplification of some SP resonance amplitudes relative to bare gold. This enhancement of the resonance may be due to the presence of an electrolyte as the ambient medium at the gold surface. The cause of this effect, however, is not relevant to our present analysis. The significant feature in our analysis, indicating the presence of inhibitor, is the level of damping of the SP resonance relative to bare gold. These resonance amplitudes are sufficient, therefore, for suggesting that the adsorbed layers have been washed off.

The trends observed in the SPR studies show reasonably good consistency with those of the weight loss studies. ADD1 and ADD5 were observed, for all experimental trials, to have SPR spectra consistent with weak or no adherence of a surface film on the gold substrate. This result is consistent with the weight loss trend observed for ADD1 and ADD5 for both metals. Relative to unaltered seawater, ADD5 is detrimental for both aluminum and steel, ADD1 is detrimental for aluminum and no better for steel. That is to say the corrosion rate of steel in seawater is about the same with or without the presence of ADD1. ADD2, ADD3 and ADD4 were observed to have a non-negligible level of SPR damping after washing with 1% NaCl relative to some of the other inhibitors tested, i.e., no shift in the minima positions. This result again is consistent with the weight loss trends, which indicate a relatively high level of corrosion protection for both metals, the exception being ADD3 for aluminum. The corrosion rates of steel and aluminum increase relative to seawater in the presence of ADD6. Although the SPR spectra for ADD6 show evidence of physical adherence, apparently the adsorbed species increases rather than decreases corrosion rates.

CONCLUSIONS

The objective of this work was to examine the intrinsic capacity of commercial rinse additives to affect corrosion rates of aluminum and steel specimens representative of materials of construction for military vehicles. Controlled laboratory exposures were designed to afford the maximum potential of the additive to reduce corrosion rates. That is, the experiments were such that it was clear that the additive could make contact with the metal surfaces or be able to affect the process leading to corrosion. This approach represents an initial step towards a quantitative assessment of whether, in fact, rinse additives have the potential to reduce corrosion rates on operational vehicles and an attempt to rank their effects for various seawater environments.

Based on the trends in our experimental results the following observations can be made.
(a) In aluminum, pitting is significantly increased in ADD1, ADD3, ADD6 and ADD5 containing seawater for all seawater concentrations. Rinses containing these additives should be avoided for aluminum parts. In the presence of ADD4 and ADD2, aluminum pits somewhat less than in seawater and these additives may be recommended for aluminum.
(b) The corrosion rate of steel is reduced in lower strength seawater. This suggests that when fresh water is scarce, rinses of exposed steel surfaces with low salinity seawater may be beneficial. ADD1, ADD6 and ADD5 provide poor protection to steel in seawater and these additives may be avoided. However significant reductions in corrosion rates are observed for ADD4, ADD3 and ADD2 and these additives may be recommended for steel.
(c) If we consider both aluminum and steel, then ADD4 and ADD2 may be recommended as wash additives.
(d) A significant, and yet somewhat subtle, result of this analysis is that it supports an increased confidence level concerning the overall concept of using inhibitor additives or reductions in seawater concentration as a viable method of corrosion control. The results demonstrate a high degree of sensitivity to differences in the types of wash down additives, and further, a marked and statistically reliable reduction in corrosion due to either the presence of inhibitor additives or reduction in seawater concentration. The effects of the additives tested show some correlation with long-term marine exposure results.
(e) SPR measurements are shown to detect the intrinsic attraction of corrosion inhibiting species at a metal surface and can be useful in monitoring relative endurance following mechanical washing procedures.
(f) Using the results from this study as a base line, follow-up work should examine the adherence of rinse additives once the aluminum and steel surfaces are dried and re-exposed to seawater as a simulated field condition.

ACKNOWLEDGMENTS

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Table 1: Inhibitor additives, manufacturer's description and recommended dilutions in seawater for rinse solutions.

Additive	Manufacturer's Description	Recommended Dilution, ml/l (oz/gal)
ADD1	Water additive for salt removal and corrosion inhibition	23.4 (2.5)
ADD2	Water based cleanser and degreaser that deposits a corrosion resistant film on metals	10.2 (1.5)
ADD3	Water additive for salt removal and corrosion inhibition	23.4 (2.5)
ADD4	Water based, protects metals against corrosive effects of fresh water, salt water and salt	15.6 (2.0) and 62.5 (8.0)
ADD5	Water additive that provide a corrosion protective film on metals	62.5 (8.0) Note: This is 4x recommended
ADD6	ADD5 plus a general purpose detergent, leaves a dry coating, protects against further exposure	62.5 (8.0)

Table 2. Raw data showing weight loss measurements.

| Sample # | Inhibitor | Dilution (oz/gal) | Strength of Seawater (fraction) | Sample Dimensions (cm) | | | Weight (g) | | Weight Loss | |
				Length	Width	Thickness	Before	After	(g)	(%)
							6061 Aluminum: Started: 09-12-02 Ended: 12-12-02			
A2#1	ADD4	8	1/1	5.044	2.500	0.3	10.23243	10.23132	0.00111	0.01084
A2#2	ADD4	8	1/1	5.058	2.494	0.3	10.09982	10.09867	0.00115	0.01138
A2#3	ADD4	8	1/1	5.130	2.601	0.3	10.74316	10.74237	0.00079	0.00735
A2#4	ADD4	8	1/2	5.067	2.533	0.3	10.39912	10.39827	0.00085	0.00817
A2#5	ADD4	8	1/2	5.045	2.537	0.3	10.36660	10.36562	0.00098	0.00945
A2#6	ADD4	8	1/2	5.045	2.569	0.3	10.44007	10.43918	0.00089	0.00852
A2#7	ADD4	8	1/4	5.040	2.525	0.3	10.35159	10.35053	0.00106	0.01023
A2#8	ADD4	8	1/4	5.087	2.494	0.3	10.13751	10.13671	0.00080	0.00789
A2#9	ADD4	8	1/4	5.035	2.387	0.3	9.77668	9.77586	0.00082	0.00838
A2#10	ADD4	2	1/1	5.034	2.437	0.3	9.81462	9.81339	0.00125	0.01274
A2#11	ADD4	2	1/1	5.104	2.518	0.3	10.36213	10.36095	0.00118	0.01138
A2#12	ADD4	2	1/1	5.030	2.500	0.3	10.22489	10.22403	0.00086	0.00841
A2#13	ADD4	2	1/2	5.031	2.545	0.3	10.35947	10.35837	0.00110	0.01061
A2#14	ADD4	2	1/2	5.035	2.464	0.3	9.88641	9.88553	0.00088	0.00890
A2#15	ADD4	2	1/2	5.039	2.54	0.3	10.24173	10.24084	0.00089	0.00868
A2#16	ADD4	2	1/4	5.076	2.552	0.3	10.49355	10.49273	0.00082	0.00781
A2#17	ADD4	2	1/4	5.057	2.564	0.3	10.53046	10.52943	0.00103	0.00978
A2#18	ADD4	2	1/4	5.024	2.526	0.3	10.28480	10.28387	0.00093	0.00904
A2#19	ADD5	8	1/1	5.021	2.475	0.3	9.99040	9.80500	0.18540	1.85578
A2#20	ADD5	8	1/1	5.043	2.476	0.3	10.14346	9.96120	0.18226	1.79682
A2#21	ADD5	8	1/1	5.055	2.499	0.3	10.26769	10.07747	0.19027	1.85309
A2#22	ADD5	8	1/2	5.014	2.554	0.3	10.27836	10.15979	0.11857	1.15358
A2#23	ADD5	8	1/2	5.049	2.568	0.3	10.13926	10.01889	0.12037	1.18716
A2#24	ADD5	8	1/2	5.035	2.495	0.3	10.08913	9.95680	0.13233	1.31160
A2#25	ADD5	8	1/4	5.072	2.542	0.3	10.28354	10.17700	0.10645	1.03514
A2#26	ADD5	8	1/4	5.132	2.526	0.3	10.37921	10.27220	0.10701	1.03100
A2#27	ADD5	8	1/4	5.030	2.427	0.3	9.91389	9.81630	0.09759	0.98437

Table 2. Continued.

Sample #	Inhibitor	Dilution (oz/gal)	Strength of Seawater (fraction)	Sample Dimensions			Weight (g)		Weight Loss	
				Length	Width	Thickness	Before	After	(g)	(%)
S2#1	ADD4	8	1/1	5.070	2.615	0.3	29.95523	29.81346	0.14177	0.47327
S2#2	ADD4	8	1/1	5.205	2.595	0.3	29.69463	29.57896	0.11567	0.38953
S2#3	ADD4	8	1/1	5.093	2.606	0.3	29.75164	29.62976	0.12188	0.40965
S2#4	ADD4	8	1/2	5.125	2.602	0.3	29.47501	29.35027	0.12474	0.42320
S2#5	ADD4	8	1/2	5.135	2.552	0.3	29.33278	29.21050	0.12228	0.41687
S2#6	ADD4	8	1/2	5.080	2.591	0.3	29.55572	29.44210	0.11362	0.38442
S2#7	ADD4	8	1/4	5.225	2.576	0.3	30.10284	29.97799	0.12485	0.41474
S2#8	ADD4	8	1/4	5.108	2.614	0.3	29.89954	29.77403	0.12551	0.41977
S2#9	ADD4	8	1/4	5.101	2.598	0.3	29.09504	28.99017	0.10487	0.36043
S2#10	ADD4	2	1/1	5.266	2.586	0.3	30.11901	29.97850	0.14051	0.46651
S2#11	ADD4	2	1/1	5.202	2.573	0.3	29.98132	29.84487	0.13645	0.45511
S2#12	ADD4	2	1/1	5.039	2.628	0.3	29.31153	29.17474	0.13679	0.46667
S2#13	ADD4	2	1/2	5.187	2.576	0.3	29.92068	29.79008	0.13060	0.43648
S2#14	ADD4	2	1/2	5.197	2.599	0.3	29.63714	29.51200	0.12514	0.42224
S2#15	ADD4	2	1/2	5.074	2.595	0.3	29.48483	29.36124	0.12359	0.41916
S2#16	ADD4	2	1/4	5.095	2.479	0.3	28.25055	28.13009	0.12046	0.42639
S2#17	ADD4	2	1/4	5.119	2.515	0.3	28.90585	28.79814	0.10771	0.37262
S2#18	ADD4	2	1/4	5.172	2.600	0.3	30.09997	29.97699	0.12298	0.40857
S2#19	ADD5	8	1/1	5.082	2.623	0.3	29.88073	29.16757	0.71316	2.38668
S2#20	ADD5	8	1/1	5.098	2.552	0.3	29.10013	28.35823	0.74190	2.54947
S2#21	ADD5	8	1/1	5.106	2.596	0.3	29.66377	28.82320	0.84057	2.83365
S2#22	ADD5	8	1/2	4.989	2.587	0.3	28.92602	28.10325	0.82277	2.84439
S2#23	ADD5	8	1/2	5.106	2.595	0.3	29.46086	28.64918	0.81168	2.75438
S2#24	ADD5	8	1/2	5.151	2.577	0.3	29.82483	28.98218	0.84265	2.82533
S2#25	ADD5	8	1/4	4.993	2.622	0.3	29.27506	28.49960	0.77548	2.64894
S2#26	ADD5	8	1/4	5.187	2.590	0.3	29.69337	28.86341	0.83029	2.79621
S2#27	ADD5	8	1/4	5.124	2.551	0.3	28.92457	28.09710	0.82747	2.86078

1018 Steel: Started: 09-12-02 Ended: 12-12-02

Table 2. Continued.

6061 Aluminum: Started: 11-02-02   Ended: 01-31-03

Sample #	Inhibitor	Dilution (oz/gal)	Strength of Seawater (fraction)	Sample Dimensions (cm)			Weight (g)		Weight Loss	
				Length	Width	Thickness	Before	After	(g)	(%)
A3#1	ADD6	8	1/1	5.015	2.500	0.3	10.04170	9.93674	0.10496	1.04524
A3#2	ADD6	8	1/1	5.053	2.512	0.3	10.33913	10.23785	0.10128	0.97957
A3#3	ADD6	8	1/1	5.096	5.542	0.3	10.31256	10.21334	0.09922	0.96212
A3#4	ADD6	8	1/2	5.110	2.570	0.3	10.61725	10.52430	0.09295	0.87546
A3#5	ADD6	8	1/2	5.110	2.520	0.3	10.36369	10.29394	0.06975	0.67302
A3#6	ADD6	8	1/2	5.080	2.420	0.3	9.90261	9.82704	0.07557	0.76313
A3#7	ADD6	8	1/4	5.020	2.520	0.3	10.14587	10.09365	0.05222	0.51469
A3#8	ADD6	8	1/4	5.070	2.470	0.3	10.12058	10.07782	0.04276	0.42250
A3#9	ADD6	8	1/4	5.120	2.570	0.3	10.66263	10.62001	0.04262	0.39971

1018 Steel: Started: 11-02-02   Ended: 01-31-03

Sample #	Inhibitor	Dilution (oz/gal)	Strength of Seawater (fraction)	Sample Dimensions (cm)			Weight (g)		Weight Loss	
				Length	Width	Thickness	Before	After	(g)	(%)
S3#1	ADD6	8	1/1	5.075	2.620	0.3	29.74952	29.34502	0.4009	1.34758
S3#2	ADD6	8	1/1	5.150	2.530	0.3	28.96560	28.55395	0.41165	1.44165
S3#3	ADD6	8	1/1	5.130	2.570	0.3	29.50898	29.09183	0.41715	1.41363
S3#4	ADD6	8	1/2	5.095	2.620	0.3	29.63377	29.22020	0.41357	1.39560
S3#5	ADD6	8	1/2	4.970	2.600	0.3	29.08813	28.64782	0.44031	1.51371
S3#6	ADD6	8	1/2	5.050	2.570	0.3	29.17995	28.75334	0.42661	1.46199
S3#7	ADD6	8	1/4	4.980	2.540	0.3	29.24328	28.88752	0.35576	1.21655
S3#8	ADD6	8	1/4	5.070	2.590	0.3	29.44877	29.09732	0.35145	1.19342
S3#9	ADD6	8	1/4	5.010	2.590	0.3	28.88216	28.53480	0.34736	1.20268

Table 2. Continued.

				6061 Aluminum:	Started: 04-18-02		Ended: 07-18-02			
Sample #	Inhibitor	Dilution (oz/gal)	Strength of Seawater (fraction)	Sample Dimensions (cm)			Weight (g)		Weight Loss	
				Length	Width	Thickness	Before	After	(g)	(%)
A1#1	seawater	control	1/2	5.041	2.435	0.322	10.28287	10.27913	0.00374	0.03637
A1#2	seawater	control	1/2	5.143	2.460	0.322	10.44891	10.44386	0.00505	0.04833
A1#3	seawater	control	1/2	5.116	2.430	0.322	10.3183	10.31374	0.00456	0.04419
A1#4	ADD2	1.5	1/2	5.159	2.444	0.322	10.47859	10.47706	0.00153	0.01460
A1#5	ADD2	1.5	1/2	5.066	2.442	0.322	10.28189	10.28116	0.00073	0.00710
A1#6	ADD2	1.5	1/2	5.115	2.467	0.322	10.55698	10.5531	0.00388	0.03675
A1#7	ADD1	2.5	1/2	5.095	2.500	0.322	10.64962	10.60445	0.04517	0.42415
A1#8	ADD1	2.5	1/2	5.032	2.442	0.322	10.24979	10.21126	0.03853	0.37591
A1#9	ADD1	2.5	1/2	5.126	2.518	0.322	10.60708	10.57168	0.03540	0.33374
A1#10	ADD3	2.5	1/2	5.124	2.425	0.322	10.34649	10.29719	0.04930	0.47649
A1#11	ADD3	2.5	1/2	5.064	2.431	0.322	10.36265	10.31864	0.04401	0.42470
A1#12	ADD3	2.5	1/2	5.150	2.443	0.322	10.48799	10.44164	0.04635	0.44193
A1#13	Seawater	control	1/4	5.044	2.426	0.322	10.2442	10.242	0.00220	0.02148
A1#14	Seawater	control	1/4	5.076	2.461	0.322	10.36849	10.36438	0.00411	0.03964
A1#15	Seawater	control	1/4	5.110	2.433	0.322	10.324	10.32001	0.00399	0.03865
A1#16	ADD2	1.5	1/4	5.113	2.452	0.322	10.38203	10.38142	0.00061	0.00588
A1#17	ADD2	1.5	1/4	5.041	2.514	0.322	10.5539	N/A	N/A	N/A
A1#18	ADD2	1.5	1/4	5.087	2.459	0.322	10.39544	10.39425	0.00119	0.01145
A1#19	ADD1	2.5	1/4	5.083	2.506	0.322	10.58413	10.52453	0.05960	0.56311
A1#20	ADD1	2.5	1/4	5.100	2.514	0.322	10.71068	10.6594	0.05128	0.47877
A1#21	ADD1	2.5	1/4	5.115	2.483	0.322	10.51117	10.45943	0.05174	0.49224
A1#22	ADD3	2.5	1/4	5.105	2.462	0.322	10.43832	10.40472	0.03360	0.32189
A1#23	ADD3	2.5	1/4	5.086	2.433	0.322	10.3188	10.28106	0.03774	0.36574
A1#24	ADD3	2.5	1/4	5.096	2.456	0.322	10.29723	10.2772	0.02003	0.19452
	Seawater	Control	1/1	N/A	N/A	N/A	N/A	N/A	N/A	0.030
	ADD2	1.5	1/1	N/A	N/A	N/A	N/A	N/A	N/A	0.005
	ADD1	2.5	1/1	N/A	N/A	N/A	N/A	N/A	N/A	0.500
	ADD3	2.5	1/1	N/A	N/A	N/A	N/A	N/A	N/A	0.565

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Table 2. Continued.

Sample #	Inhibitor	Dilution (oz/gal)	Strength of Seawater (fraction)	Sample Dimensions (cm)			Weight (g)		Weight Loss	
				Length	Width	Thickness	Before	After	(g)	(%)
S1#1	Seawater	control	1/2	5.160	2.515	0.298	29.15593	28.89922	0.25671	0.88047
S1#2	Seawater	control	1/2	5.100	2.480	0.298	28.37745	28.10574	0.27171	0.95749
S1#3	Seawater	control	1/2	5.030	2.480	0.298	28.07861	N/A	N/A	N/A
S1#4	ADD2	1.5	1/2	5.095	2.547	0.298	29.1122	28.90101	0.21119	0.72543
S1#5	ADD2	1.5	1/2	5.166	2.550	0.298	29.24307	29.03979	0.20328	0.69514
S1#6	ADD2	1.5	1/2	5.095	2.530	0.298	28.98365	28.80275	0.18090	0.62414
S1#7	ADD1	2.5	1/2	5.085	2.498	0.298	28.23359	27.96921	0.26438	0.93640
S1#8	ADD1	2.5	1/2	5.150	2.492	0.298	28.7689	28.4919	0.27700	0.96285
S1#9	ADD1	2.5	1/2	5.080	2.550	0.298	28.9675	28.69535	0.27215	0.93950
S1#10	ADD3	2.5	1/2	5.138	2.468	0.298	28.5932	28.48015	0.11305	0.39537
S1#11	ADD3	2.5	1/2	5.100	2.478	0.298	28.35662	28.23663	0.11999	0.42315
S1#12	ADD3	2.5	1/2	5.112	2.523	0.298	28.89663	28.7906	0.10603	0.36693
S1#13	Seawater	control	1/4	5.165	2.475	0.298	28.5579	28.2698	0.28810	1.00883
S1#14	Seawater	control	1/4	5.246	2.506	0.298	29.66177	N/A	N/A	N/A
S1#15	Seawater	control	1/4	5.155	2.533	0.298	29.23266	28.94854	0.28412	0.97193
S1#16	ADD2	1.5	1/4	5.160	2.491	0.298	28.6704	28.4955	0.17490	0.61004
S1#17	ADD2	1.5	1/4	5.136	2.511	0.298	29.10491	28.92962	0.17529	0.60227
S1#18	ADD2	1.5	1/4	5.116	2.460	0.298	28.186669	28.00749	0.17918	0.63569
S1#19	ADD1	2.5	1/4	5.136	2.477	0.298	28.45048	28.18184	0.26864	0.94424
S1#20	ADD1	2.5	1/4	5.144	2.472	0.298	28.30869	28.04868	0.26001	0.91848
S1#21	ADD1	2.5	1/4	5.212	2.476	0.298	29.22095	28.95343	0.26752	0.91551
S1#22	ADD3	2.5	1/4	5.135	2.536	0.298	29.0166	28.91136	0.10524	0.36269
S1#23	ADD3	2.5	1/4	5.220	2.475	0.298	28.9947	28.87451	0.12019	0.41452
S1#24	ADD3	2.5	1/4	5.175	2.476	0.298	28.68452	28.57529	0.10923	0.38080
	Seawater	Control	1/1	N/A	N/A	N/A	N/A	N/A	N/A	1.800
	ADD2	1.5	1/1	N/A	N/A	N/A	N/A	N/A	N/A	0.750
	ADD1	2.5	1/1	N/A	N/A	N/A	N/A	N/A	N/A	1.450
	ADD3	2.5	1/1	N/A	N/A	N/A	N/A	N/A	N/A	0.300

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Table. 3: Weight loss results for 6061 aluminum showing averages and standard deviations (S.D.)

Seawater Strength / Inhibitor	Full (1/1)		Half (1/2)		Quarter (1/4)	
	Average (%)	S.D.	Average (%)	S.D.	Average (%)	S.D.
ADD1	0.50320	0.0000	0.37793	0.045239	0.51137	0.045309
ADD2	0.0020000	0.0000	0.019483	0.015416	0.0086650	0.0039386
ADD3	0.56470	0.0000	0.44771	0.026374	0.29405	0.088940
ADD4 (2)	0.010843	0.0022143	0.0093967	0.0010565	0.0088333	0.0012341
ADD4 (8)	0.0098567	0.0021876	0.0087133	0.0006615	0.0088767	0.0009951
ADD5	1.8352	0.033312	1.2175	0.083235	1.0168	0.028180
ADD6	0.99563	0.043807	0.77054	0.10142	0.44563	0.060881
Seawater Control	*0.029000*	*0.0000*	*0.042963*	*0.0060736*	*0.033257*	*0.010211*

Table 4: Weight loss results for 1018 steel showing averages and standard deviations (S.D.)

Seawater Strength / Inhibitor	Full (1/1)		Half (1/2)		Quarter (1/4)	
	Average (%)	S.D.	Average (%)	S.D.	Average (%)	S.D.
ADD1	1.4290	0.0000	0.94625	0.014459	0.92608	0.015800
ADD2	0.74290	0.0000	0.68157	0.051991	0.61600	0.017489
ADD3	0.29500	0.0000	0.39515	0.028111	0.38600	0.026304
ADD4 (2)	0.46276	0.0066285	0.42596	0.0092398	0.40253	0.027390
ADD4 (8)	0.42415	0.043713	0.40816	0.020804	0.39831	0.032904
ADD5	2.5900	0.22623	2.8080	0.047419	2.7686	0.10861
ADD6	1.4010	0.048305	1.4571	0.059202	1.2042	0.011623
Seawater Control	*1.8043*	*0.0000*	*0.91898*	*0.054461*	*0.99037*	*0.026071*

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Table 5: Average weight loss relative to seawater control.

Seawater Strength \\ Inhibitor	6061 Aluminum			1018 Steel		
	Full (1/1)	Half (1/2)	Quarter (1/4)	Full (1/1)	Half (1/2)	Quarter (1/4)
ADD1	17.35	8.80	15.38	0.79	1.03	0.94
ADD2	0.07	0.45	0.26	0.41	0.74	0.62
ADD3	19.47	10.42	8.84	0.16	0.43	0.39
ADD4 (2)	0.37	0.22	0.27	0.26	0.46	0.41
ADD4 (8)	0.34	0.20	0.27	0.24	0.44	0.40
ADD5	63.28	28.34	30.57	1.44	3.06	2.80
ADD6	34.33	17.93	13.40	0.78	1.59	1.22

Table 6. Analysis of SPR spectra giving position or scan angle, θ (°) and amplitude or (-R) of the minima. 'None' means no minima.

Substrate	Bare Gold		No Wash		Water Wash		NaCl Wash	
	θ (°)	(-R)	θ (°)	(-R)	θ (°)	(-R)	θ (°)	(-R)
Bare Gold	46.5	0.57	--	--	46.5	0.70	48.5	0.44
ADD1	46.4	0.56	46.8	0.33	46.6	0.41	47.9	0.54
ADD2	46.5	0.57	None	None	47.0	0.36	47.0	0.39
ADD3	46.4	0.56	None	None	46.6	0.36	46.6	0.35
Bare Gold	46.3	0.46	--	--	46.5	0.44	47.7	0.39
ADD4	46.3	0.47	None	None	46.7	0.45	46.8	0.40
ADD5	46.5	0.46	42.7	0.17	46.5	0.44	46.5	0.45
ADD6	46.4	0.50	None	None	46.4	0.48	47.6	0.42

Table 7: Ratio of average weight loss in steel to the average weight loss in aluminum.

Seawater Strength / Inhibitor	1018 Steel / 6061 Aluminum		
	Full (1/1)	Half (1/2)	Quarter (1/4)
ADD1	2.8	2.5	1.8
ADD2	371.5	35.0	71.1
ADD3	0.52	0.88	1.31
ADD4 (2)	42.7	45.3	45.6
ADD4 (8)	43.0	46.8	44.9
ADD5	1.4	2.3	2.7
ADD6	1.4	1.9	2.7
Seawater Control	62.2	21.4	29.8

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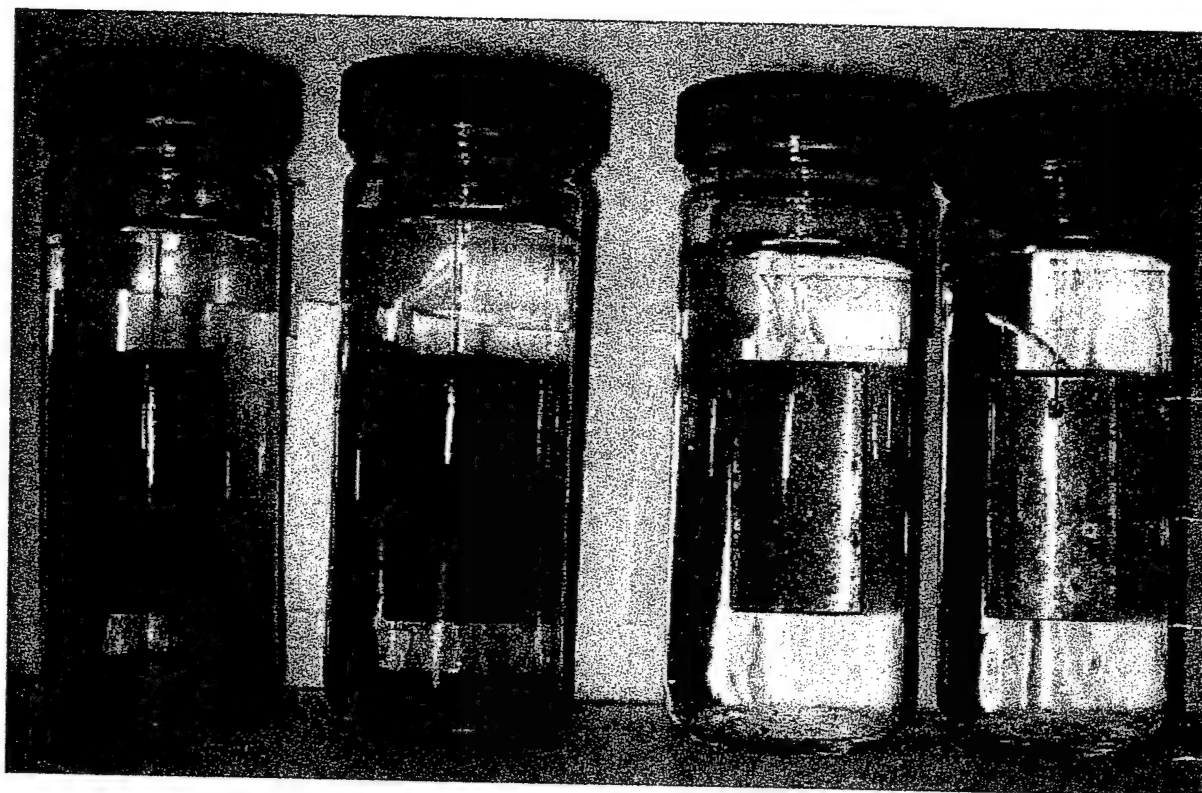
Figure 1. Test set-up for evaluating the influence of inhibitor additives on corrosion processes in seawater. Sample bottles from left to right, 1018 steel in 1/4 and 1/2 strength seawater, 6061 aluminum in 1/4 and 1/2 strength seawater.
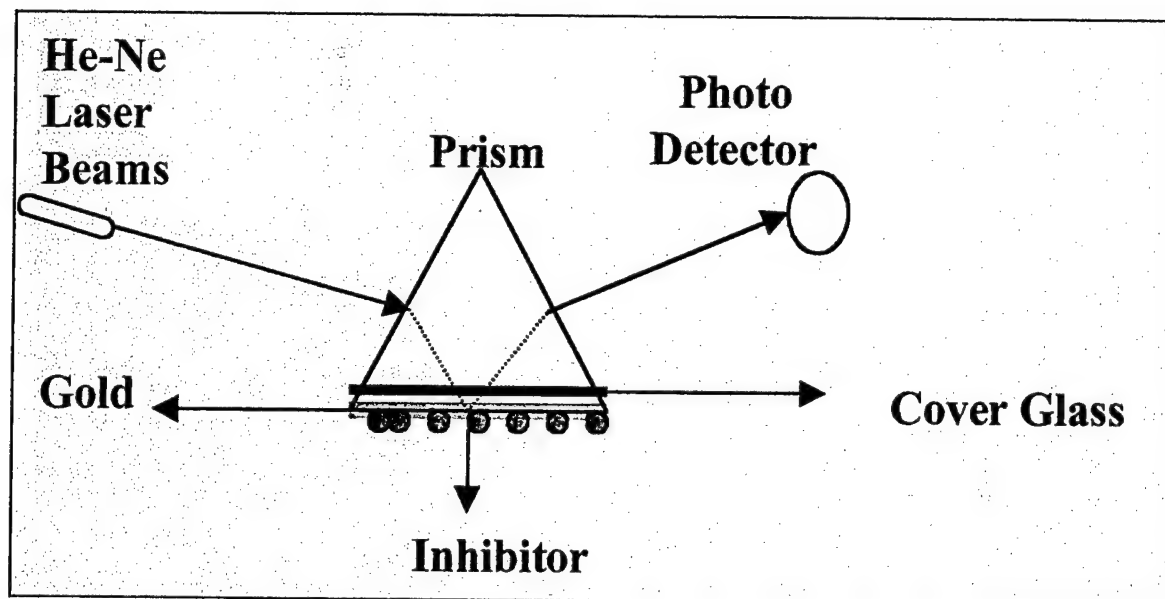
Figure 2. Schematic representation of experimental arrangement for surface plasmon resonance (SPR) spectroscopy measurements designed to determine inhibitor adherence.
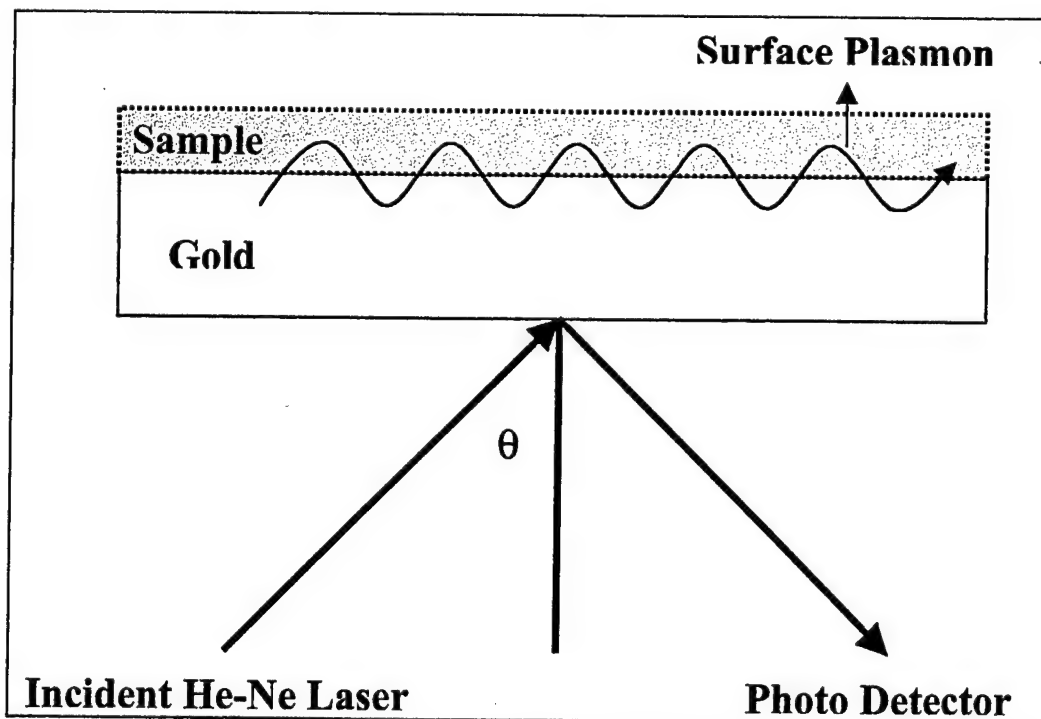
Figure 3. Schematic diagram describing SPR measurement and interpretation of results.
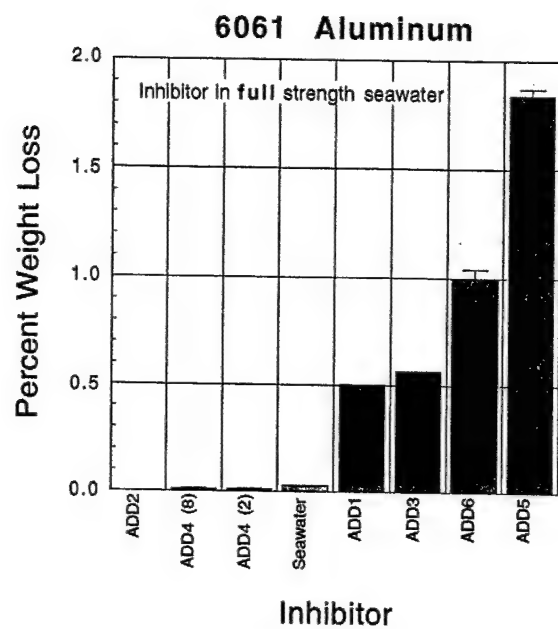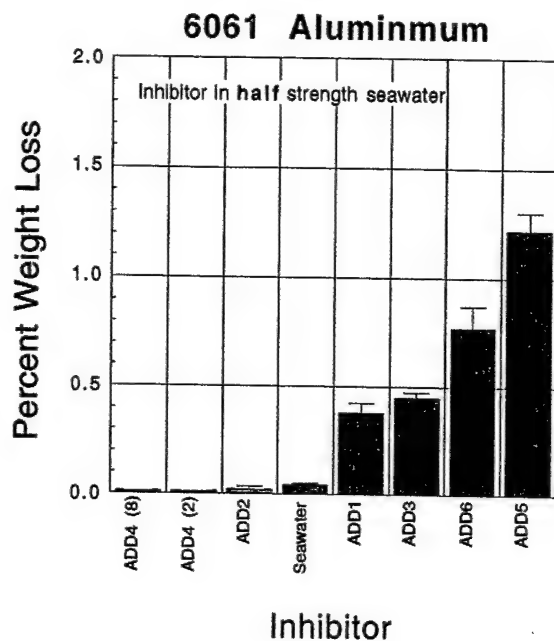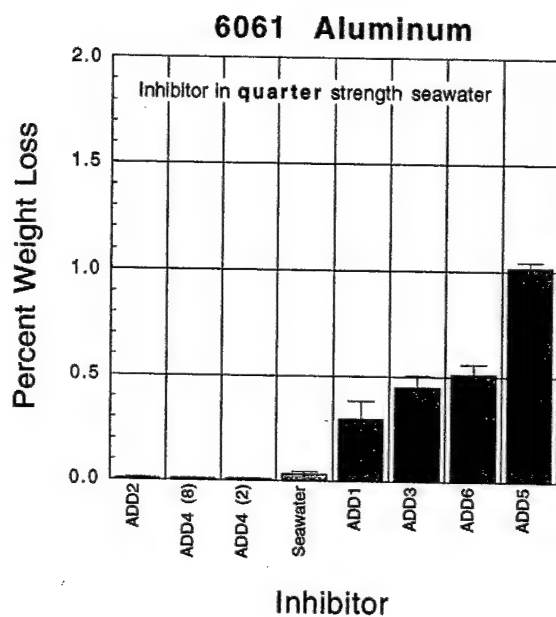
Figure 4. Inhibitor rankings relative to seawater control for aluminum based on weight loss measurements. **(a)** Full strength seawater. **(b)** Half strength seawater. **(c)** Quarter strength seawater.
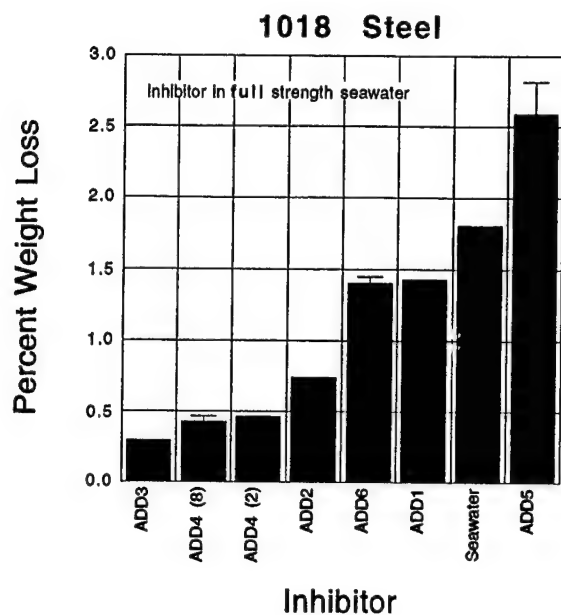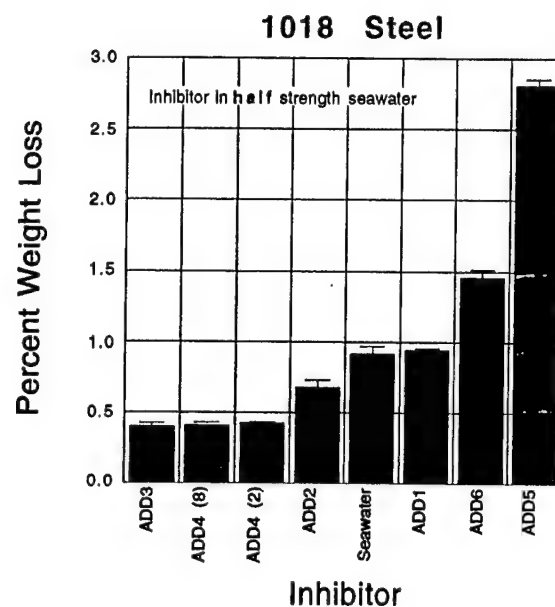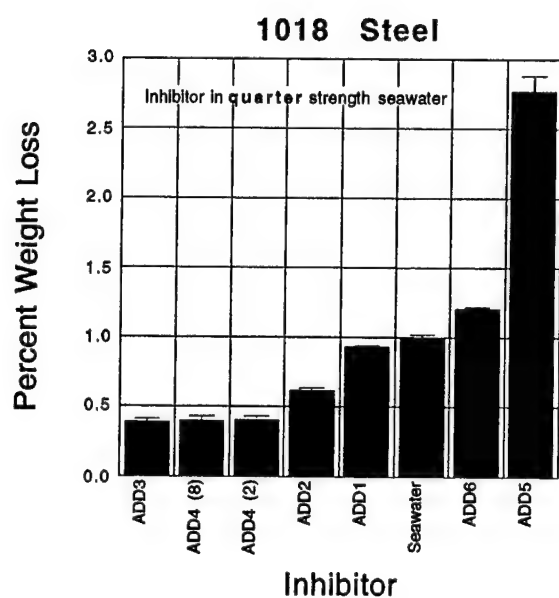
Figure 5: Inhibitor rankings relative to seawater control for steel based on weight loss measurements. **(a)** Full strength seawater. **(b)** Half strength seawater. **(c)** Quarter strength seawater.
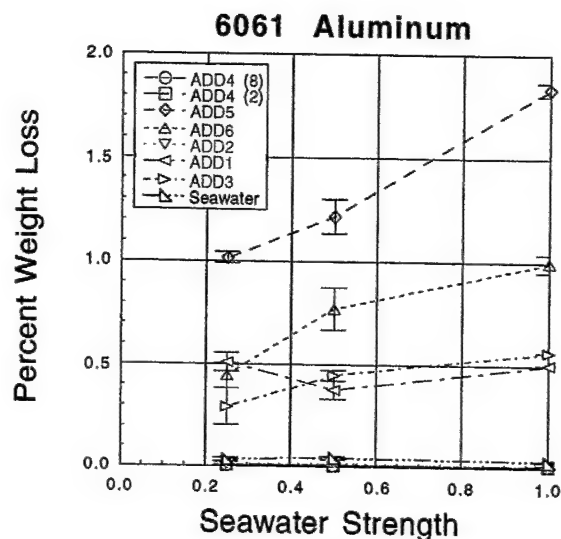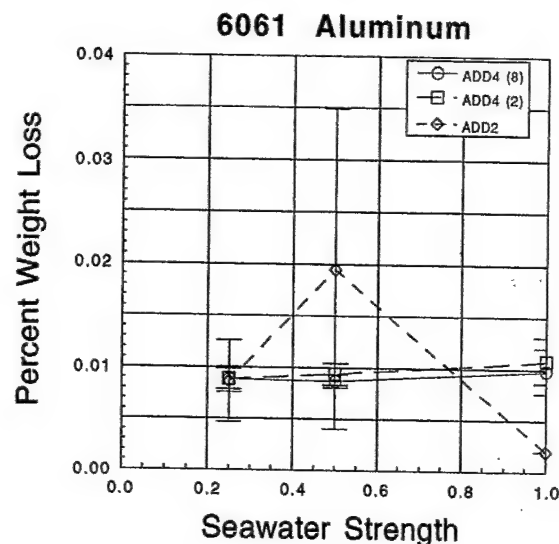
Figure 6. (a) Effect of inhibitor additives and seawater control on the weight loss of aluminum as a function of seawater strength. **(b)** Graph amplifying effects observed with additives resulting in least weight loss.
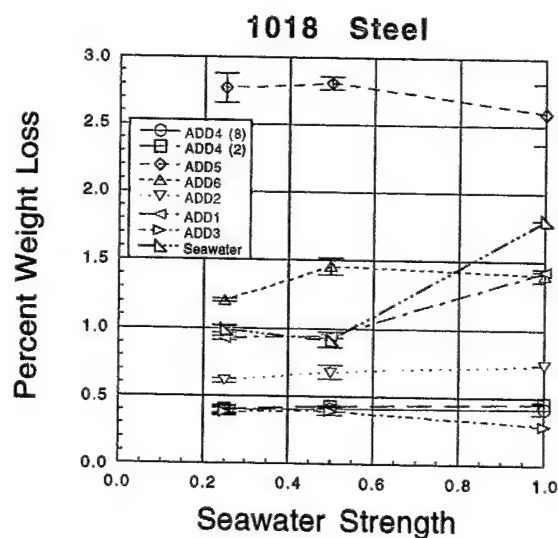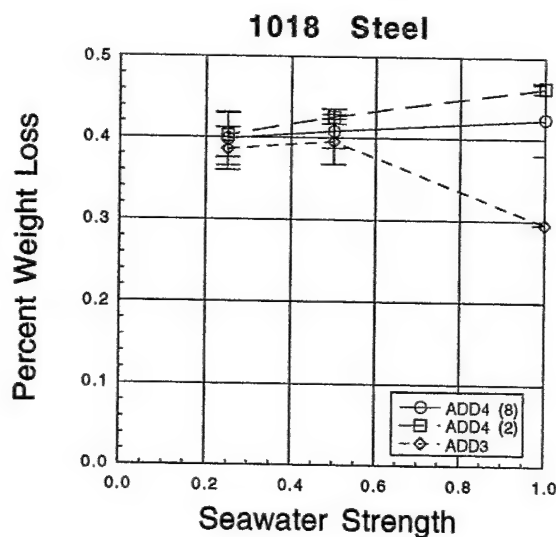
Figure 7. (a) Effect of inhibitor additives and seawater control on the weight loss of steel as a function of seawater strength. **(b)** Graph amplifying effects observed with additives resulting in least weight loss.
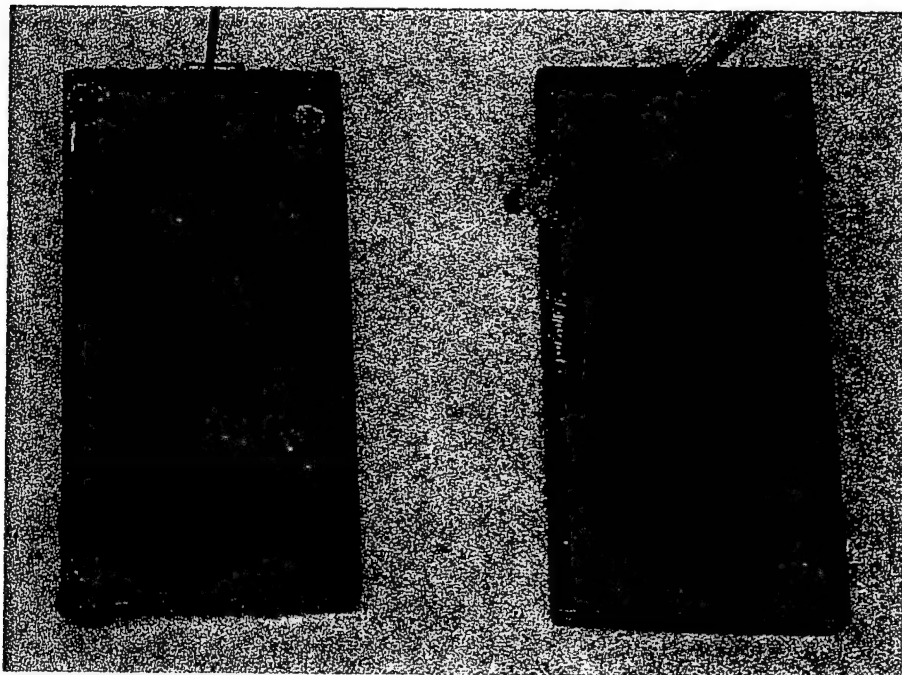
Figure 8. Comparison of the extent of pitting in aluminum alloy coupons following immersion in seawater containing ADD3 (left) and seawater without an additive (right).
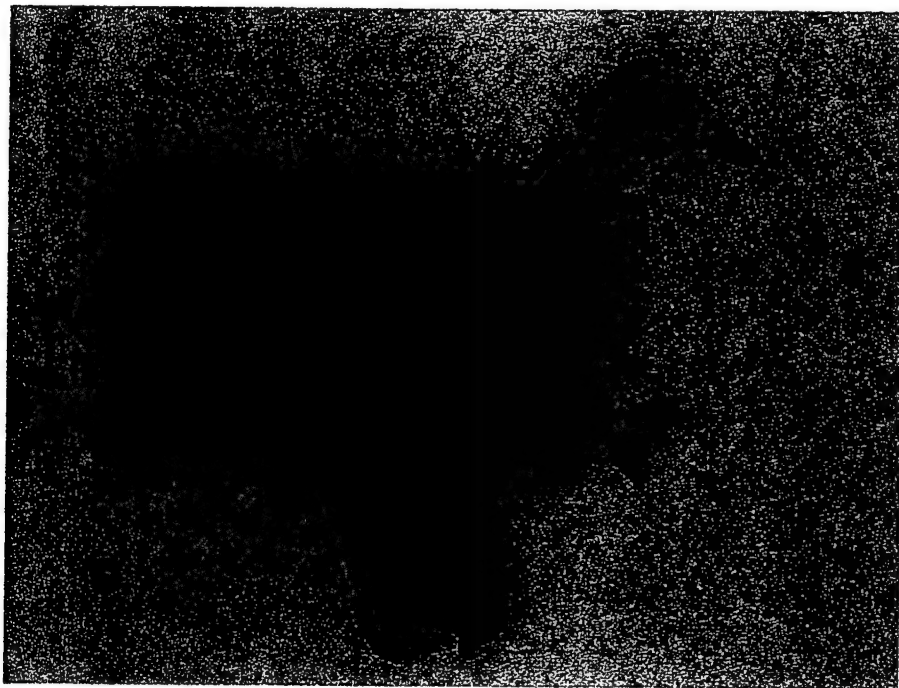
Figure 9. Corrosion product shown pealing off a steel coupon immersed in seawater containing ADD6.
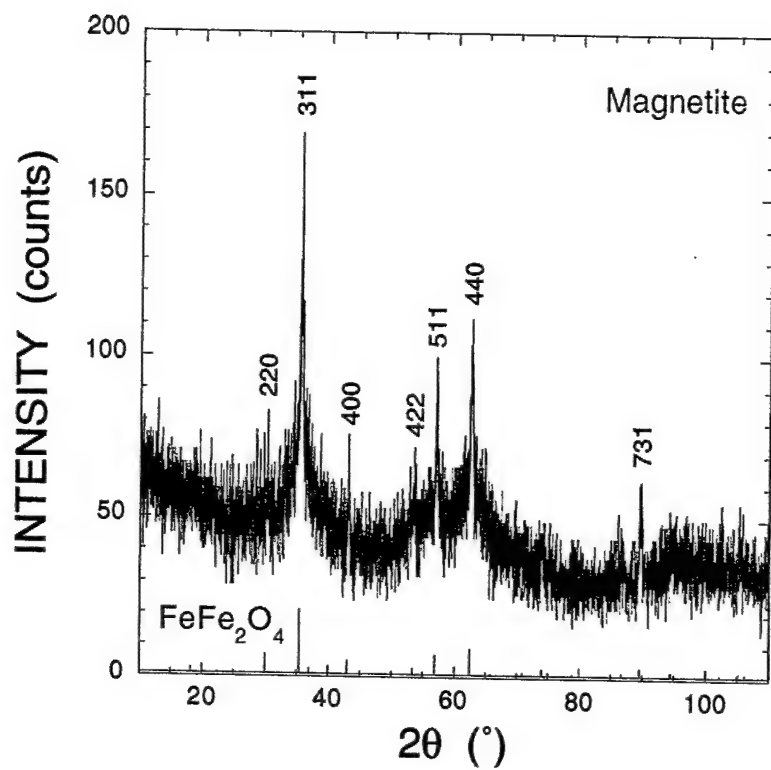
Figure 10. X-ray diffraction spectrum of corrosion product formed on the surface of steel coupon immersed in seawater containing ADD6 inhibitor. Superimposed are the reflections of the $FeFe_2O_4$ standard.
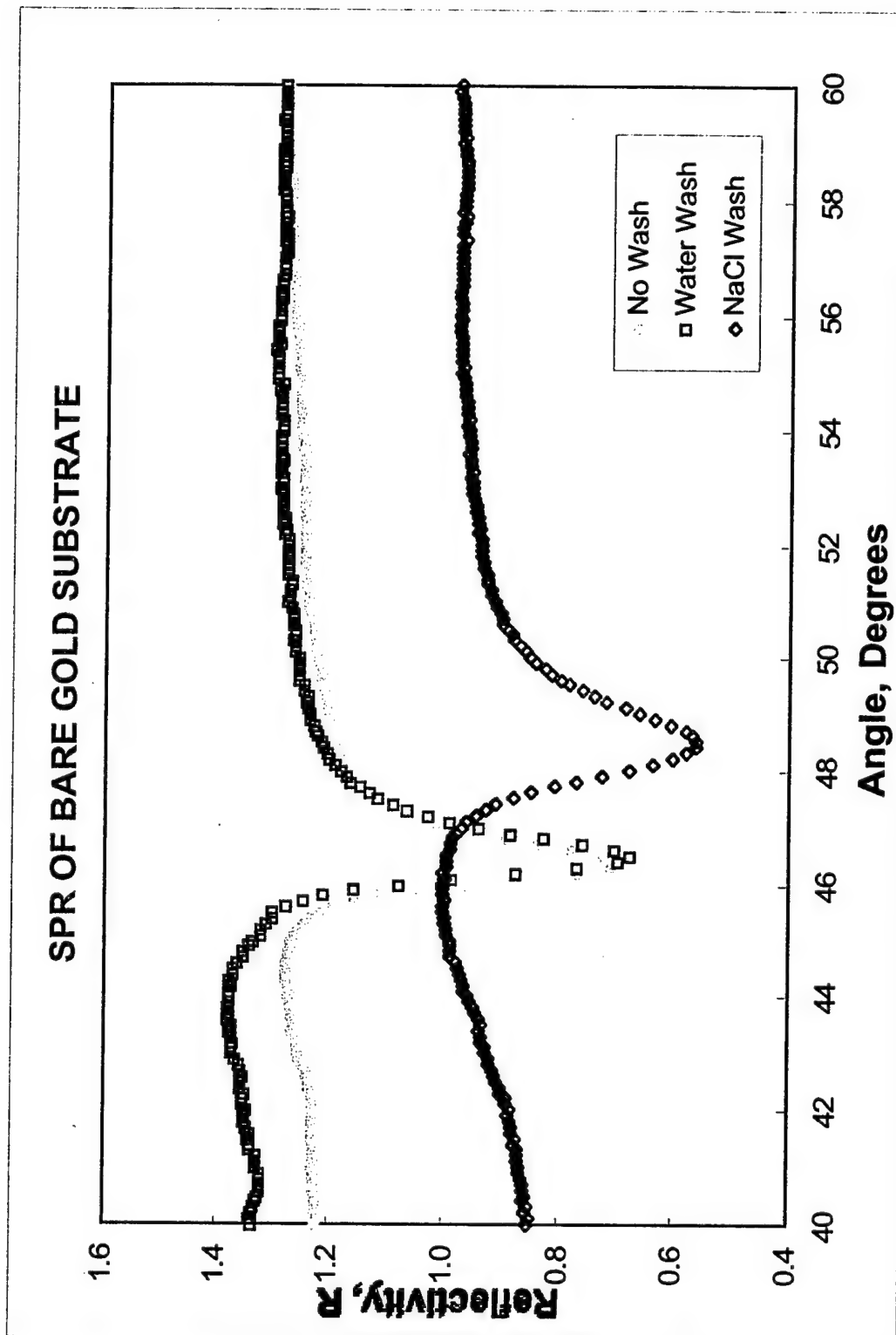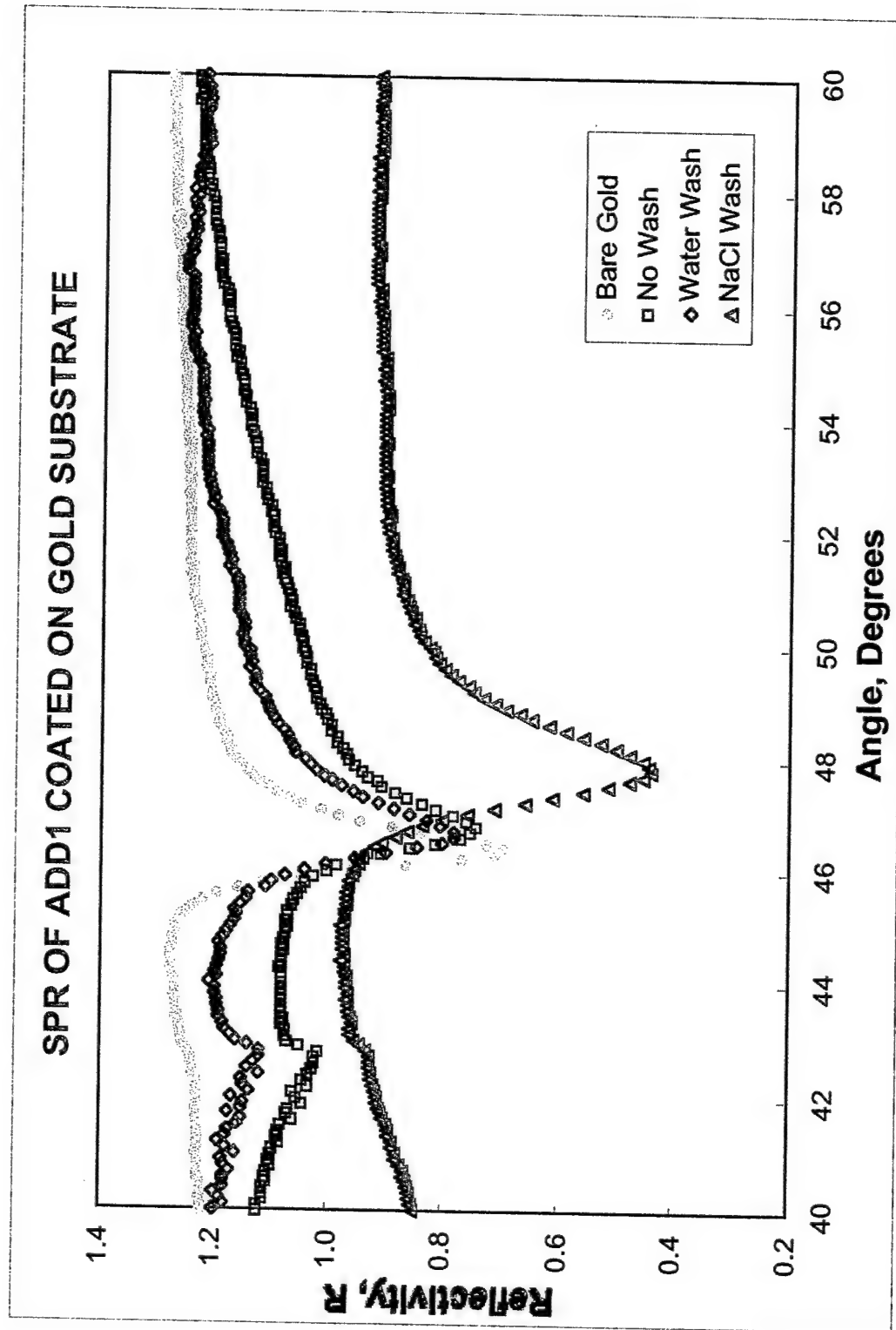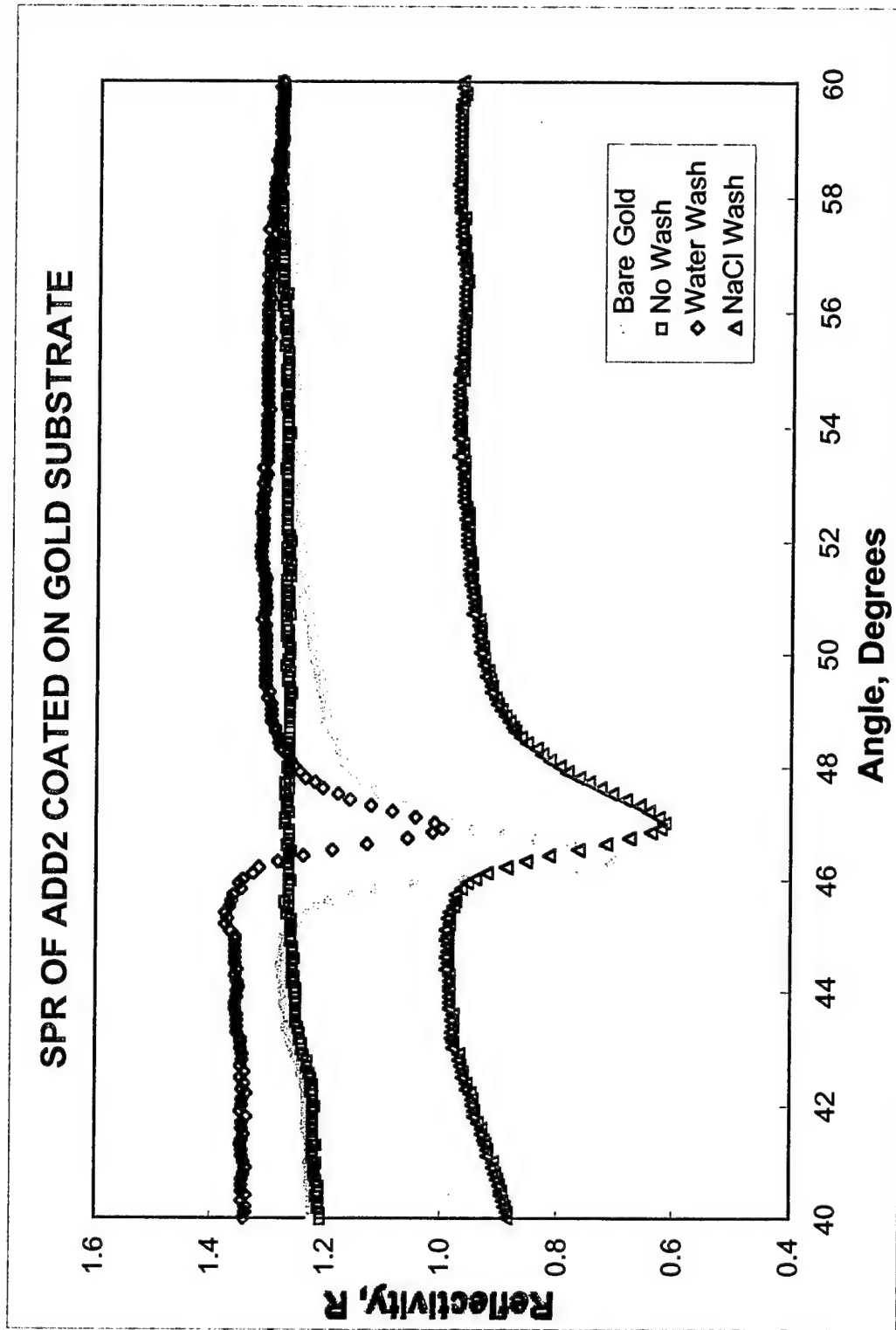
SPR OF BARE GOLD SUBSTRATE

Reflectivity, R

Angle, Degrees

- No Wash
- □ Water Wash
- ◇ NaCl Wash

Figure 11. (a)

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SPR OF ADD1 COATED ON GOLD SUBSTRATE

Bare Gold
No Wash
Water Wash
NaCl Wash

Reflectivity, R

Angle, Degrees

Figure 11. (b)

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SPR OF ADD2 COATED ON GOLD SUBSTRATE

Legend:
Bare Gold
□ No Wash
◇ Water Wash
△ NaCl Wash

Reflectivity, R

Angle, Degrees

Figure 11. (c)

34
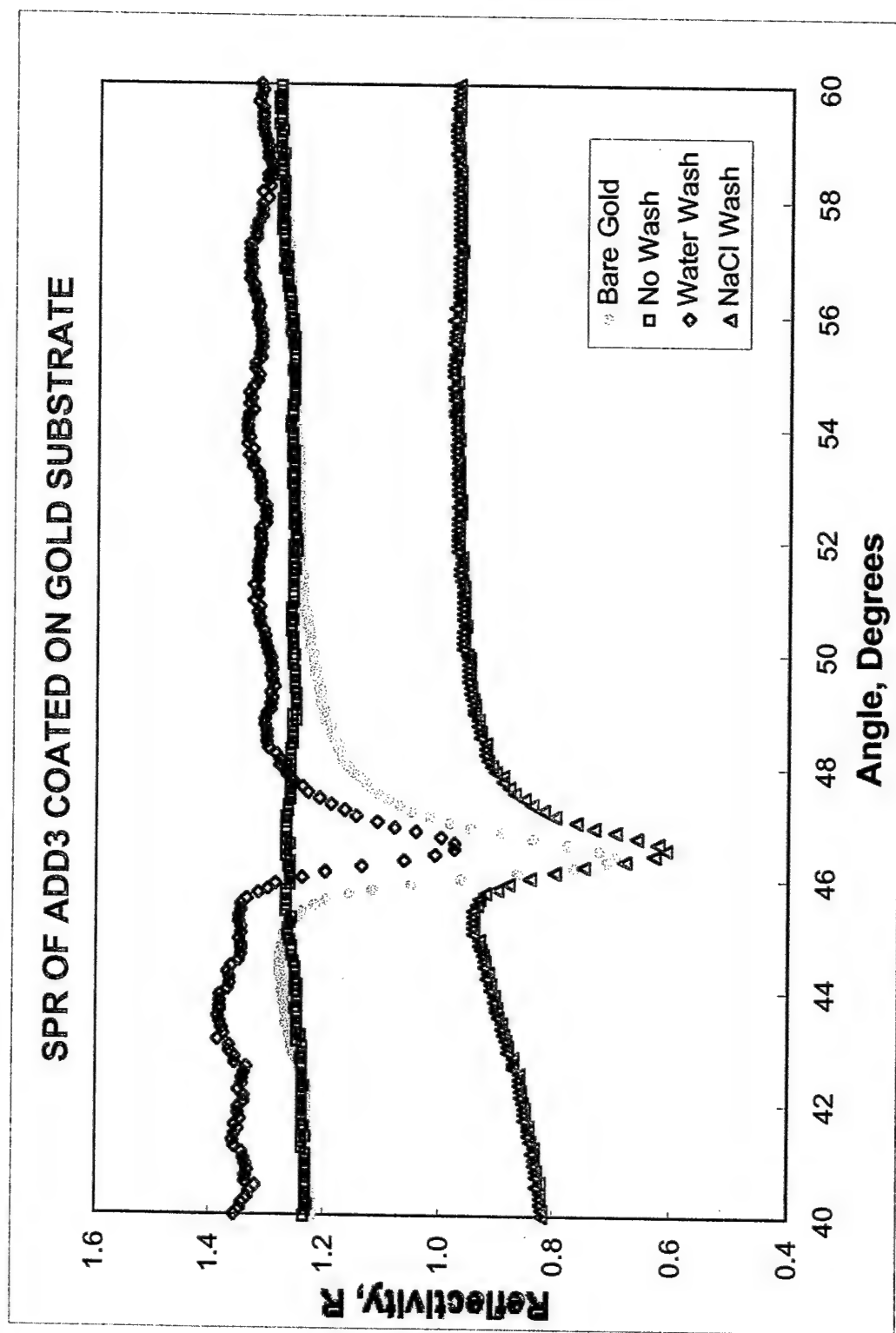
Figure 11. SPR spectra of bare gold substrate, with inhibitor coating and after washing inhibitor coated substrate with water and 1.0% NaCl. **(a)** Bare gold substrate. **(b)** ADD1 coated substrate. **(c)** ADD2 coated substrate. **(d)** ADD3 coated substrate.
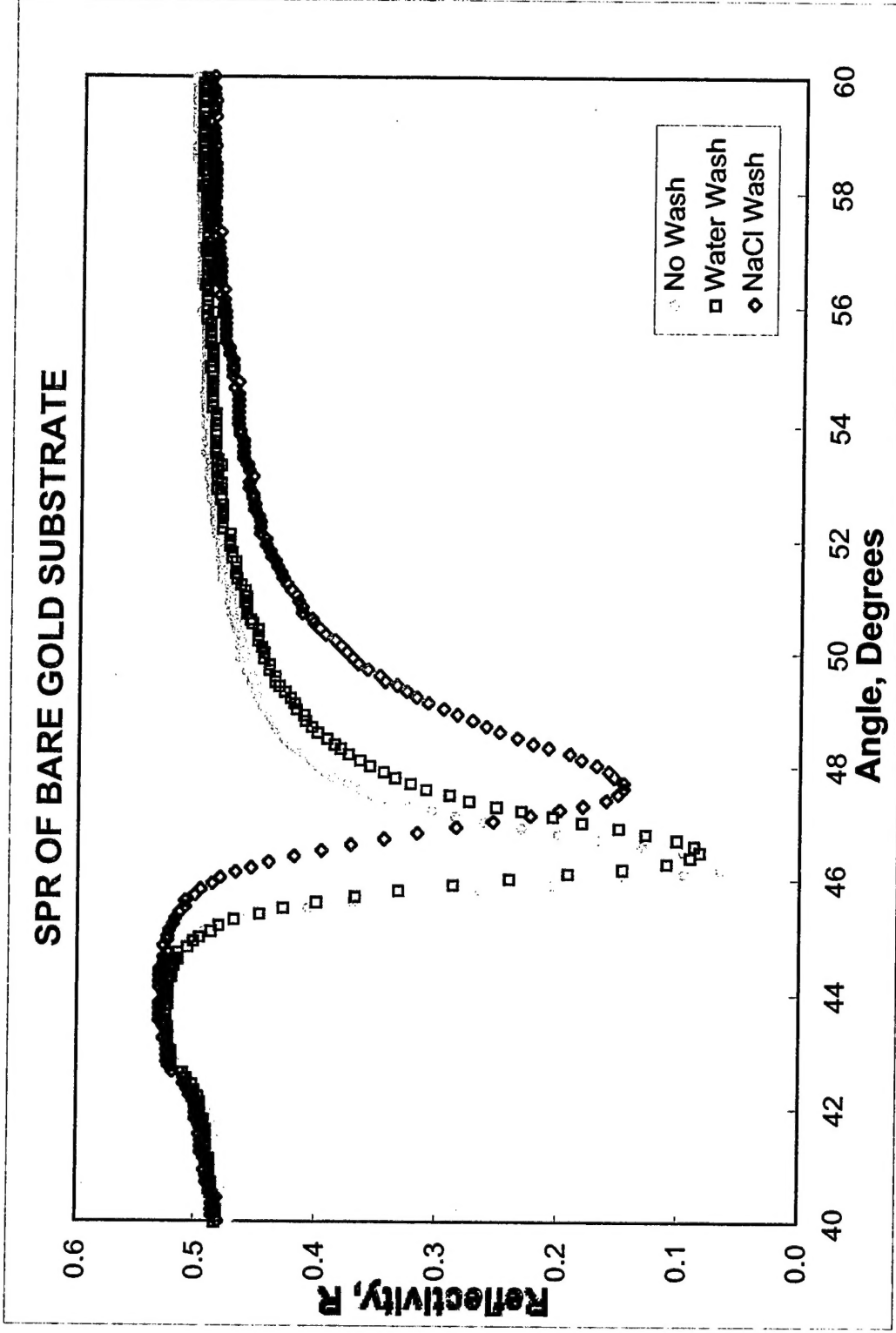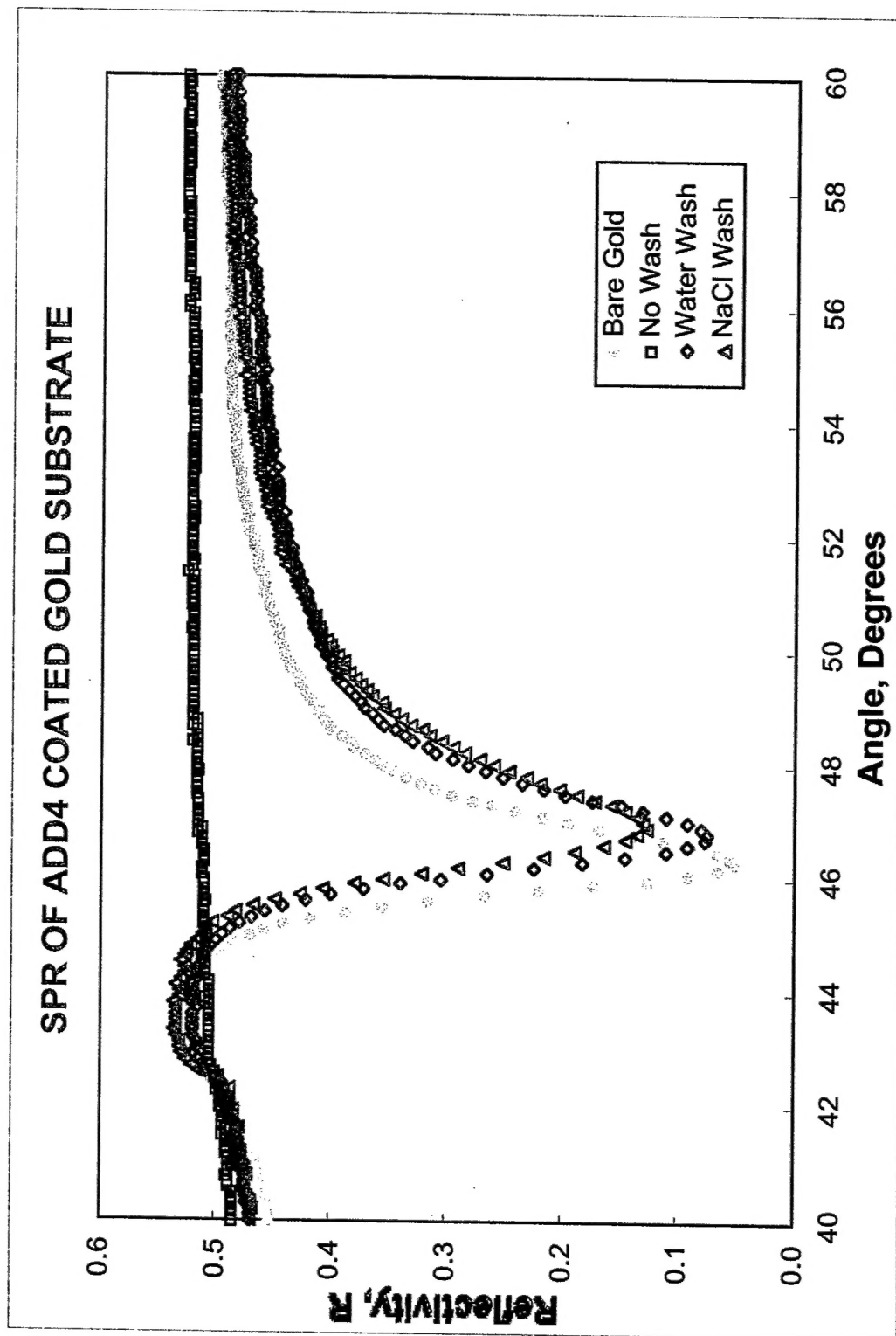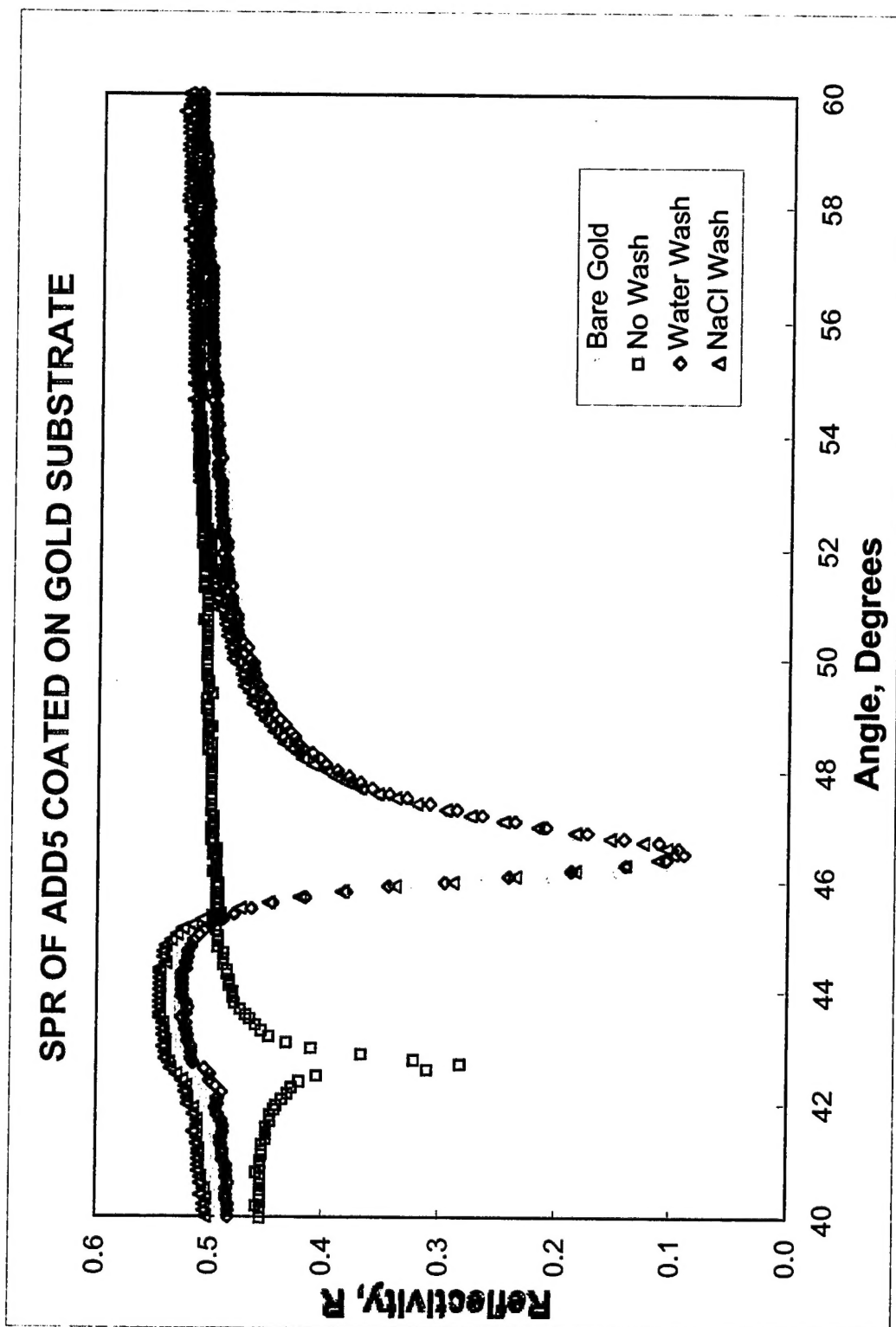
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Figure 12. (a)

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SPR OF ADD4 COATED GOLD SUBSTRATE

Figure 12. (b)

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SPR OF ADD5 COATED ON GOLD SUBSTRATE

Angle, Degrees

Reflectivity, R

Legend:
- Bare Gold
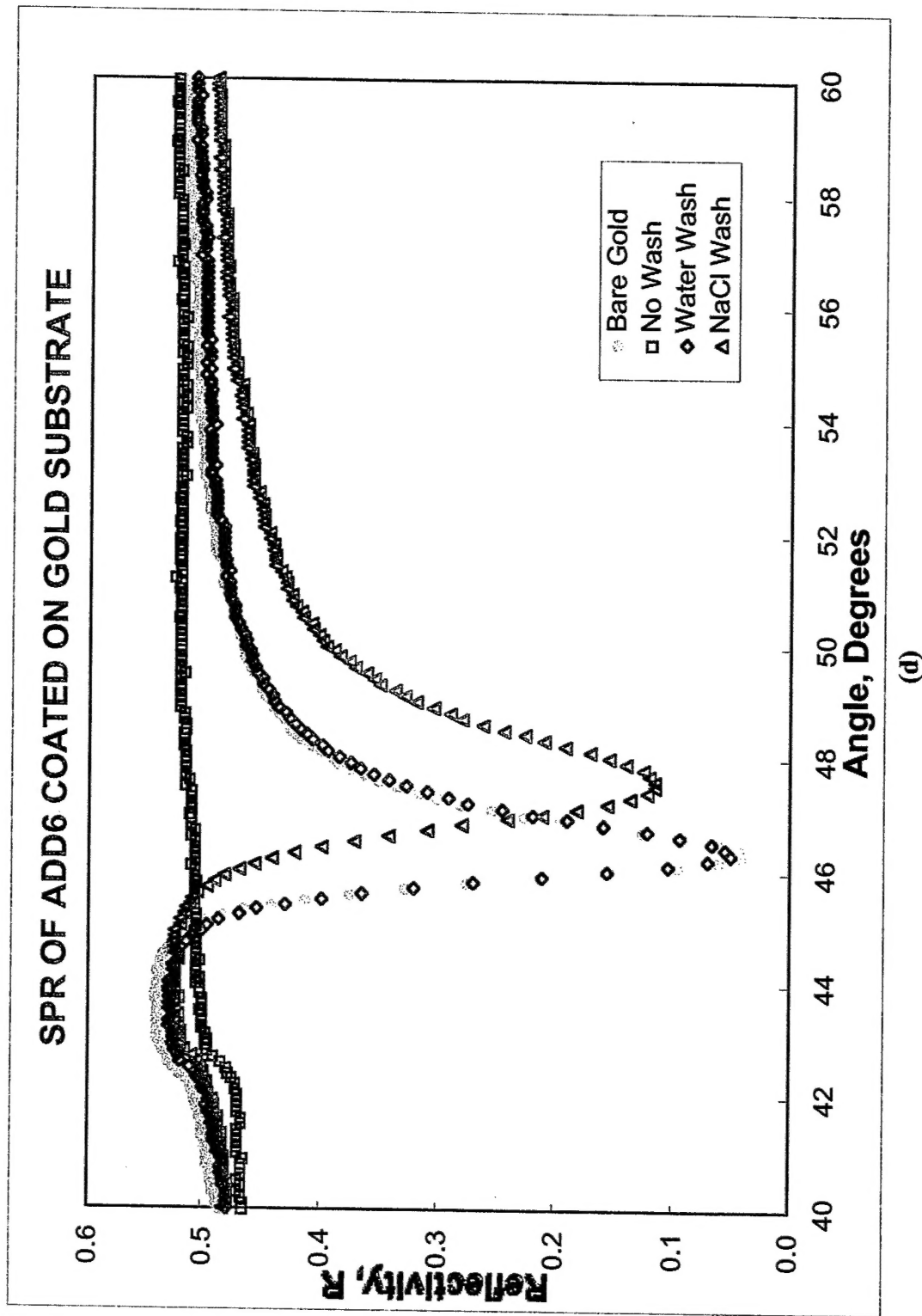- No Wash
- Water Wash
- NaCl Wash

Figure 12. (c)

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Figure 12. SPR spectra of bare gold substrate, with inhibitor coating and after washing inhibitor coated substrate with water and 1.0% NaCl. **(a)** Bare gold substrate. **(b)** ADD4 coated substrate. **(c)** ADD5 coated substrate. **(d)** ADD6 coated substrate.

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